



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
-----------------	-------------	----------------------	---------------------	------------------

09/914,966

09/06/2001

Larry Neil Mackey

U 013595-2

6640

27752

7590

02/12/2008

THE PROCTER & GAMBLE COMPANY
INTELLECTUAL PROPERTY DIVISION - WEST BLDG.
WINTON HILL BUSINESS CENTER - BOX 412
6250 CENTER HILL AVENUE
CINCINNATI, OH 45224

EXAMINER

JUSKA, CHERYL ANN

ART UNIT

PAPER NUMBER

1794

MAIL DATE

DELIVERY MODE

02/12/2008

PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

09/914966

Examiner: JUSKA, CHERYL

GAU: 1794




















Inventor: MACKEY, LARRY, et al

Classification: 442/327.000

Status: 124 - ON APPEAL -- AWAITING DECISION BY THE BOARD OF APPEALS

Title: ABSORBENT, FLEXIBLE, STRUCTURE COMPRISING STARCH FIBERS

PROSECUTION tab report (119 items, sorted by Date DESC)

Img	Status	Doc Code	Document Type	Date	Pages	Annotations
	13	M327	Miscellaneous Communication to Applicant - No Action Count	11/07/2007	2	
	13	1449	List of References cited by applicant and considered by examiner	11/07/2007	1	
	7	APRD	Order Returning Undocketed Appeal to the examiner from BPAI	10/18/2007	2	return order
	7	RBNE	Reply Brief Noted - BPAI	07/27/2007	2	reply brief noted
	7	APRB	Reply Brief Filed	05/11/2007	5	reply brief
	7	APOH	Request for Oral Hearing	05/11/2007	1	request for oral hearing
	7	TRTC	Transmittal to TC	05/11/2007	1	
	7	FWCLM	Index of Claims	03/12/2007	1	
	7	APEA	Examiner's Answer to Appeal Brief	03/12/2007	11	examiners anwser
	7	AP.B	Appeal Brief Filed	10/06/2006	16	appeal brief
	7	CTMS	Miscellaneous Action with SSP	09/08/2006	2	non-compliant appeal brief
	7	AP.B	Appeal Brief Filed	06/26/2006	16	
	7	APOH	Request for Oral Hearing	06/26/2006	3	request for oral hearing
	7	N/AP	Notice of Appeal Filed	04/25/2006	3	notice of appeal-Appeal no. 2008-1716.
	7	CTAV	Advisory Action (PTOL-303)	04/14/2006	3	
	7	FWCLM	Index of Claims	04/14/2006	1	
	7	ANE.I	Amendment After Final or under 37CFR 1.312, initialed by the examiner.	04/14/2006	1	do not enter per examiner
	7	A.NE	Amendment After Final	04/10/2006	2	
	7	REM	Applicant Arguments/Remarks Made in an Amendment	04/10/2006	2	

09/914966

Examiner: JUSKA, CHERYL

GAU: 1794

Inventor: MACKEY, LARRY, et al

Classification: 442/327.000

Status: 124 - ON APPEAL -- AWAITING DECISION BY THE BOARD OF APPEALS

Title: ABSORBENT, FLEXIBLE, STRUCTURE COMPRISING STARCH FIBERS

PROSECUTION tab report (119 items, sorted by Date DESC)

Img	Status	Doc Code	Document Type	Date	Pages	Annotations
	7	CLM.NE	Claim-Amendment Not Entered	04/10/2006	3	
	7	WFEE	Fee Worksheet (PTO-06)	04/10/2006	1	
	7	FWCLM	Index of Claims	02/09/2006	1	
	7	CTFR	Final Rejection	02/09/2006	7	final rejection
	7	AMSB	Amendment Submitted/Entered with Filing of CPA/RCE	12/07/2005	1	
	7	CLM	Claims	12/07/2005	3	
	7	REM	Applicant Arguments/Remarks Made in an Amendment	12/07/2005	3	
	7	TRTC	Transmittal to TC	12/07/2005	1	
	7	RCEX	Request for Continued Examination (RCE)	12/07/2005	1	
	7	AF/D	Rule 130, 131 or 132 Affidavits	12/07/2005	4	
	7	WFEE	Fee Worksheet (PTO-06)	12/07/2005	1	
	7	WFEE	Fee Worksheet (PTO-06)	12/07/2005	2	
	7	CTAV	Advisory Action (PTOL-303)	11/02/2005	3	
	7	ANE.I	Amendment After Final or under 37CFR 1.312, initialed by the examiner.	11/02/2005	1	
	7	FWCLM	Index of Claims	11/02/2005	1	
	7	A.NE	Amendment After Final	10/21/2005	2	
	7	REM	Applicant Arguments/Remarks Made in an Amendment	10/21/2005	2	
	7	CLM.NE	Claim-Amendment Not Entered	10/21/2005	3	
	7	WFEE	Fee Worksheet (PTO-06)	10/21/2005	1	
	7	CTFR	Final Rejection	09/16/2005	5	

09/914966

Examiner: JUSKA, CHERYL

GAU: 1794

Inventor: MACKEY, LARRY, et al

Classification: 442/327.000

Status: 124 - ON APPEAL -- AWAITING DECISION BY THE BOARD OF APPEALS

Title: ABSORBENT, FLEXIBLE, STRUCTURE COMPRISING STARCH FIBERS

PROSECUTION tab report (119 items, sorted by Date DESC)

Img	Status	Doc Code	Document Type	Date	Pages	Annotations
	7	FWCLM	Index of Claims	09/16/2005	1	
	7	WFEE	Fee Worksheet (PTO-06)	07/13/2005	1	
	7	A...	Amendment - After Non-Final Rejection	06/29/2005	2	<FAX>
	7	CLM	Claims	06/29/2005	3	
	7	REM	Applicant Arguments/Remarks Made in an Amendment	06/29/2005	2	
	7	CTNF	Non-Final Rejection	04/07/2005	6	
	7	FWCLM	Index of Claims	04/07/2005	1	
	7	AMSB	Amendment Submitted/Entered with Filing of CPA/RCE	03/06/2005	1	
	7	CLM	Claims	03/06/2005	3	
	7	REM	Applicant Arguments/Remarks Made in an Amendment	03/06/2005	3	
	7	TRTC	Transmittal to TC	03/06/2005	1	
	7	RCEX	Request for Continued Examination (RCE)	03/06/2005	1	
	7	WFEE	Fee Worksheet (PTO-06)	03/06/2005	1	
	7	CTFR	Final Rejection	12/10/2004	6	
	7	FWCLM	Index of Claims	12/10/2004	1	
	7	SRFW	Search information including classification, databases and other search related notes	12/10/2004	1	
	7	SRNT	Examiner's search strategy and results	12/08/2004	1	
	7	WFEE	Fee Worksheet (PTO-06)	09/30/2004	1	
	7	A...	Amendment - After Non-Final Rejection	09/27/2004	4	
	7	CLM	Claims	09/27/2004	3	

09/914966

Examiner: JUSKA, CHERYL

GAU: 1794



















Inventor: MACKEY, LARRY, et al

Classification: 442/327.000

Status: 124 - ON APPEAL -- AWAITING DECISION BY THE BOARD OF APPEALS

Title: ABSORBENT, FLEXIBLE, STRUCTURE COMPRISING STARCH FIBERS

PROSECUTION tab report (119 items, sorted by Date DESC)

Img	Status	Doc Code	Document Type	Date	Pages	Annotations
	7	CTMS	Miscellaneous Action with SSP	09/20/2004	2	
	7	A...	Amendment - After Non-Final Rejection	08/18/2004	2	
	7	CLM	Claims	08/18/2004	2	
	7	REM	Applicant Arguments/Remarks Made in an Amendment	08/18/2004	3	
	7	TRTC	Transmittal to TC	08/18/2004	1	
	7	CTNF	Non-Final Rejection	07/02/2004	10	
	7	FWCLM	Index of Claims	07/02/2004	1	
	7	TRTC	Transmittal to TC	04/28/2004	1	
	7	RCEX	Request for Continued Examination (RCE)	04/19/2004	2	
	7	CTAV	Advisory Action (PTOL-303)	03/31/2004	3	
	7	ANE.I	Amendment After Final or under 37CFR 1.312, initialed by the examiner.	03/31/2004	1	
	7	SRFW	Search information including classification, databases and other search related notes	03/31/2004	1	
	7	REM	Applicant Arguments/Remarks Made in an Amendment	03/18/2004	4	
	7	ANE.I	Amendment After Final or under 37CFR 1.312, initialed by the examiner.	03/18/2004	2	
	7	SPEC.NE	Specification-Amendment Not Entered	03/18/2004	1	
	7	CLM.NE	Claim-Amendment Not Entered	03/18/2004	2	
	7	IDS	Information Disclosure Statement (IDS) Filed	03/12/2004	6	
	7	IDS	Information Disclosure Statement (IDS) Filed	02/02/2004	3	
	7	CTFR	Final Rejection	01/21/2004	8	

09/914966

Examiner: JUSKA, CHERYL

GAU: 1794




















Inventor: MACKEY, LARRY, et al

Classification: 442/327.000

Status: 124 - ON APPEAL -- AWAITING DECISION BY THE BOARD OF APPEALS

Title: ABSORBENT, FLEXIBLE, STRUCTURE COMPRISING STARCH FIBERS

PROSECUTION tab report (119 items, sorted by Date DESC)

Img	Status	Doc Code	Document Type	Date	Pages	Annotations
	7	FWCLM	Index of Claims	01/21/2004	1	
	7	BIB	Bibliographic Data Sheet	01/21/2004	1	
	7	SRFW	Search information including classification, databases and other search related notes	01/21/2004	1	
	7	SRNT	Examiner's search strategy and results	01/09/2004	1	
	7	SRNT	Examiner's search strategy and results	01/07/2004	3	
	7	A...	Amendment - After Non-Final Rejection	10/02/2003	1	
	7	REM	Applicant Arguments/Remarks Made in an Amendment	10/02/2003	5	Amendments to Title, Spec and claims here.
	7	IDS	Information Disclosure Statement (IDS) Filed	10/02/2003	3	
	7	IDS	Information Disclosure Statement (IDS) Filed	07/24/2003	3	
	7	CTNF	Non-Final Rejection	07/01/2003	11	
	7	LET.	Miscellaneous Incoming Letter	06/23/2003	1	
	7	IDS	Information Disclosure Statement (IDS) Filed	04/18/2003	2	
	7	IDS	Information Disclosure Statement (IDS) Filed	03/18/2003	2	
	7	IDS	Information Disclosure Statement (IDS) Filed	02/11/2003	2	
	7	IDS	Information Disclosure Statement (IDS) Filed	12/11/2002	2	
	7	IDS	Information Disclosure Statement (IDS) Filed	09/30/2002	2	
	7	IDS	Information Disclosure Statement (IDS) Filed	06/25/2002	4	
	7	C.AD	Change of Address	05/10/2002	1	
	7	IDS	Information Disclosure Statement (IDS) Filed	04/15/2002	4	

09/914966

Examiner: JUSKA, CHERYL

GAU: 1794

Inventor: MACKEY, LARRY, et al

Classification: 442/327.000

Status: 124 - ON APPEAL -- AWAITING DECISION BY THE BOARD OF APPEALS

Title: ABSORBENT, FLEXIBLE, STRUCTURE COMPRISING STARCH FIBERS

PROSECUTION tab report (119 items, sorted by Date DESC)

Img	Status	Doc Code	Document Type	Date	Pages	Annotations
	7	IDS	Information Disclosure Statement (IDS) Filed	02/12/2002	4	
	7	IDS	Information Disclosure Statement (IDS) Filed	02/05/2002	4	
	7	IDS	Information Disclosure Statement (IDS) Filed	01/30/2002	4	
	7	PA..	Power of Attorney	01/30/2002	1	
	7	M903	Notice of DO/EO Acceptance Mailed	10/26/2001	2	
	7	TRNA	Transmittal of New Application	09/06/2001	8	
	7	CLM	Claims	09/06/2001	2	
	7	DRW	Drawings-only black and white line drawings	09/06/2001	7	
	7	OATH	Oath or Declaration filed	09/06/2001	2	
	7	SPEC	Specification	09/06/2001	57	
	7	BIB	Bibliographic Data Sheet	09/06/2001	2	
	7	IDS	Information Disclosure Statement (IDS) Filed	09/06/2001	2	
	7	SRNT	Examiner's search strategy and results	09/06/2001	1	
	7	IMIS	Miscellaneous Internal Document	09/06/2001	1	
	7	WCLM	Claims Worksheet (PTO-2022)	09/06/2001	1	
	7	WFEE	Fee Worksheet (PTO-06)	09/06/2001	1	
	7	IIFW	Issue Information including classification, examiner, name, claim, renumbering, etc.	09/06/2001	1	
	7	SRFW	Search information including classification, databases and other search related notes	09/06/2001	1	
	7	FWCLM	Index of Claims	09/06/2001	1	

09/914966

Examiner: JUSKA, CHERYL

GAU: 1794




Inventor: MACKEY, LARRY, et al

Classification: 442/327.000

Status: 124 - ON APPEAL -- AWAITING DECISION BY THE BOARD OF APPEALS

Title: ABSORBENT, FLEXIBLE, STRUCTURE COMPRISING STARCH FIBERS

PROSECUTION tab report (119 items, sorted by Date DESC)

Img	Status	Doc Code	Document Type	Date	Pages	Annotations
	7	A.PE	Preliminary Amendment	09/06/2001	2	
	7	TRNA	Transmittal of New Application	09/06/2001	1	
	7	ARTIFACT	Artifact sheet indicating an item has been filed which cannot be scanned	09/06/2001	1	ordered 10/17/07 jgr



United States Patent and Trademark Office

**Under Secretary of Commerce for Intellectual Property and
Director of the United States Patent and Trademark Office**

**P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov**

THE PROCTER & GAMBLE COMPANY
INTELLECTUAL PROPERTY DIVISION - WEST BLDG.
WINTON HILL BUSINESS CENTER - BOX 412
6250 CENTER HILL AVENUE
CINCINNATI, OH 45224

Appeal No: 2008-1716
Application: 09/914,966
Appellant: Larry Neil Mackey et al.

Board of Patent Appeals and Interferences Docketing Notice

Application 09/914,966 was received from the Technology Center at the Board on January 24, 2008 and has been assigned Appeal No: 2008-1716.

A review of the file indicates that the following documents have been filed by appellant:

Appeal Brief filed on: October 06, 2006
Reply Brief filed on: May 11, 2007
Request for Hearing filed on: May 11, 2007

In all future communications regarding this appeal, please include both the application number and the appeal number.

The mailing address for the Board is:

BOARD OF PATENT APPEALS AND INTERFERENCES
UNITED STATES PATENT AND TRADEMARK OFFICE
P.O. BOX 1450
ALEXANDRIA, VIRGINIA 22313-1450

The facsimile number of the Board is 571-273-0052. Because of the heightened security in the Washington D.C. area, facsimile communications are recommended. Telephone inquiries can be made by calling 571-272-9797 and should be directed to a Program and Resource Administrator.

By order of the Board of Patent Appeals and Interferences



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
 United States Patent and Trademark Office
 Address: COMMISSIONER FOR PATENTS
 P.O. Box 1450
 Alexandria, Virginia 22313-1450
 www.uspto.gov

BIB DATA SHEET

CONFIRMATION NO. 6640

SERIAL NUMBER	FILING or 371(c) DATE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
09/914,966	09/06/2001	524	1794	U 013595-2
RULE				
APPLICANTS Larry Neil Mackey, Fairfield, OH; James Daniel Miller II, Cincinnati, OH; Mark Ryan Richards, Middletown, OH; John Gerhard Michael, Cincinnati, OH; David William Cabell, Cincinnati, OH; Valerie Ann Bailey, Florence, KY;				
** CONTINUING DATA ***** This application is a 371 of PCT/IB00/00234 03/07/2000 which is a CIP of 09/264,401 03/08/1999 ABN				
** FOREIGN APPLICATIONS *****				
** IF REQUIRED, FOREIGN FILING LICENSE GRANTED **				
Foreign Priority claimed <input type="checkbox"/> Yes <input type="checkbox"/> No	<input type="checkbox"/> Met after Allowance	STATE OR COUNTRY	SHEETS DRAWINGS	TOTAL CLAIMS
35 USC 119(a-d) conditions met <input type="checkbox"/> Yes <input type="checkbox"/> No	Initials	OH	7	10
Verified and Acknowledged	Examiner's Signature			INDEPENDENT CLAIMS
				3
ADDRESS THE PROCTER & GAMBLE COMPANY INTELLECTUAL PROPERTY DIVISION - WEST BLDG. WINTON HILL BUSINESS CENTER - BOX 412 6250 CENTER HILL AVENUE CINCINNATI, OH 45224 UNITED STATES				
TITLE Absorbent, flexible, structure comprising starch fibers				
FILING FEE RECEIVED 690	FEES: Authority has been given in Paper No. _____ to charge/credit DEPOSIT ACCOUNT No. _____ for following:	<input type="checkbox"/> All Fees		
		<input type="checkbox"/> 1.16 Fees (Filing)		
		<input type="checkbox"/> 1.17 Fees (Processing Ext. of time)		
		<input type="checkbox"/> 1.18 Fees (Issue)		
		<input type="checkbox"/> Other _____		
		<input type="checkbox"/> Credit		

Application Number Information

Application Number: 09/914966

[Assignments](#)Filing or 371(c) Date: 09/06/2001 [eDan](#)

Effective Date: 09/06/2001

Application Received: 09/06/2001

Patent Number:

Issue Date: 00/00/0000

Date of Abandonment: 00/00/0000

Attorney Docket Number: U 013595-2

Status: 124 /ON APPEAL -- AWAITING DECISION BY THE BOARD OF APPEALS

Confirmation Number: 6640

Examiner Number: 74170 / [JUSKA, CHERYL](#)

Group Art Unit: 1794

[IFW Madras](#)

Class/Subclass: 442/327.000

Lost Case: NO

Appeal Number: 20081716

Unmatched Petition: NO

[L&R Code](#): [Secrecy Code](#):1

Third Level Review: NO

Secrecy Order: NO

Status Date: 02/11/2008

Oral Hearing: YES

Title of Invention: ABSORBENT, FLEXIBLE, STRUCTURE COMPRISING STARCH FIBERS

Bar Code	PALM Location	Location Date	Charge to Loc	Charge to Name	Employee Name	Location
09914966CA	06B0	08/07/2003	No Charge to Location	No Charge to Name	PAK,TAE	
09914966ZA	28C1	10/18/2007	44P0	GUNTER RILEY, JOYCE	OUDOM,VIENXAY	RND/00/A 41

Appln
Info[Contents](#)[Petition Info](#)[Atty/Agent Info](#)[Continuity/Reexam](#)[Foreign Data](#)Search Another: Application # or Patent# PCT / / or PG PUBS # Attorney Docket # Bar Code #

To go back, right click here and select Back. To go forward, right click here and select Forward. To refresh, right click here and select Refresh.

Back to [OASIS](#) | [Home page](#)http://EXPOWEB1:8001/cgi-bin/expo/GenInfo/snquery.pl?APPL_ID=09914966



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
-----------------	-------------	----------------------	---------------------	------------------

09/914,966

09/06/2001

Larry Neil Mackey

U 013595-2

6640

27752

7590

11/07/2007

THE PROCTER & GAMBLE COMPANY
INTELLECTUAL PROPERTY DIVISION - WEST BLDG.
WINTON HILL BUSINESS CENTER - BOX 412
6250 CENTER HILL AVENUE
CINCINNATI, OH 45224

EXAMINER

JUSKA, CHERYL ANN

ART UNIT

PAPER NUMBER

1794

MAIL DATE

DELIVERY MODE

11/07/2007

PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

**UNITED STATES DEPARTMENT OF COMMERCE****U.S. Patent and Trademark Office**

Address : COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450

APPLICATION NO./ CONTROL NO.	FILING DATE	FIRST NAMED INVENTOR / PATENT IN REEXAMINATION	ATTORNEY DOCKET NO.
09914966	9/6/01	MACKEY ET AL.	U 013595-2

THE PROCTER & GAMBLE COMPANY
INTELLECTUAL PROPERTY DIVISION - WEST BLDG.
WINTON HILL BUSINESS CENTER - BOX 412
6250 CENTER HILL AVENUE
CINCINNATI, OH 45224

EXAMINER

Cheryl Juska

ART UNIT	PAPER
1794	20071106

DATE MAILED:

Please find below and/or attached an Office communication concerning this application or proceeding.

Commissioner for Patents

In response to the "Order Returning Undocketed Appeal to Examiner" mailed October 18, 2007, the Information Disclosure Statement filed September 6, 2001, has been considered. Note that all the references cited on said IDS are duplicates of those cited and previously considered on the IDS of January 30, 2002.

/Cheryl Juska/
Primary Examiner
Art Unit 1794

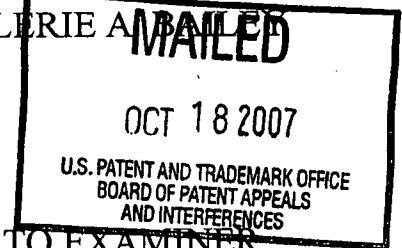
UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE BOARD OF PATENT APPEALS
AND INTERFERENCES

Ex parte : LARRY N. MACKEY, JAMES D. MILLER II, MARK R. RICHARDS,
JOHN G. MICHAEL, DAVID W. CABELL and VALERIE A. BARNES

Application No. 09/914,966

ORDER RETURNING UNDOCKETED APPEAL TO EXAMINER



This application was received electronically at the Board of Patent Appeals and Interferences on October 15, 2007. A review of the application has revealed that the application is not ready for docketing as an appeal. Accordingly, the application is herewith being returned to the examiner. The matter requiring attention prior to docketing is identified below.

An Information Disclosure Statement (IDS) was filed on September 06, 2001. A review of the Image File Wrapper reveals that the examiner has not considered the IDS. According to MPEP § 609 which states:

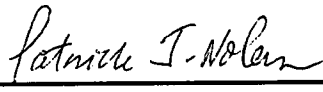
“ The Examiner must also fill in his or her name and the date the information was considered in blocks at the bottom of the PTO-1449 or PTO/SB/08A and 08B form.”

Application No. 09/914,966

Accordingly, it is

ORDERED that the application is returned to the Examiner for consideration of the IDS, written notification to the applicant of such consideration and for further action as may be appropriate.

BOARD OF PATENT APPEALS
AND INTERFERENCES

By: 
PATRICK J. NOLAN
Deputy Chief Appeals Administrator
(571) 272-9797

PJN/jgr

THE PROCTER & GAMBLE COMPANY
INTELLECTUAL PROPERTY DIVISION
WEST BLDG
WINTON HILL BUSINESS CENTER
BOX 412
6250 CENTER HILL AVENUE
CINCINNATI OH 45224



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
-----------------	-------------	----------------------	---------------------	------------------

09/914,966

09/06/2001

Larry Neil Mackey

U 013595-2

6640

27752

7590

07/27/2007

THE PROCTER & GAMBLE COMPANY
INTELLECTUAL PROPERTY DIVISION - WEST BLDG.
WINTON HILL BUSINESS CENTER - BOX 412
6250 CENTER HILL AVENUE
CINCINNATI, OH 45224

EXAMINER

JUSKA, CHERYL ANN

ART UNIT

PAPER NUMBER

1771

MAIL DATE

DELIVERY MODE

07/27/2007

PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

**UNITED STATES DEPARTMENT OF COMMERCE****U.S. Patent and Trademark Office**

Address: COMMISSIONER FOR PATENTS

P.O. Box 1450

Alexandria, Virginia 22313-1450

APPLICATION NO./ CONTROL NO.	FILING DATE	FIRST NAMED INVENTOR / PATENT IN REEXAMINATION	ATTORNEY DOCKET NO.
---------------------------------	-------------	---	---------------------

EXAMINER

ART UNIT

PAPER

20070717

DATE MAILED:

Please find below and/or attached an Office communication concerning this application or proceeding.

Commissioner for Patents

The Reply Brief filed on 05/11/07 has been entered and considered but no further response by the Examiner is deemed necessary. The application has been forwarded to the Board of Patent Appeals and Interferences for decision on the appeal.

CHERYL A. JUSKA
PRIMARY EXAMINER

Cheryl Juska
Primary Examiner
Art Unit: 1771

MAY 11 2007

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No. : 09/914,966
Applicant(s) : LARRY NEIL MACKEY et al.
Filed : September 6, 2001
TC/A.U. : 1771
Examiner : Cheryl Ann Juska
Conf. No. : 6640
Docket No. : 7456R
Customer No. : 27752
Title : ABSORBENT FLEXIBLE STRUCTURE
: COMPRISING STARCH FIBERS

REPLY BRIEF UNDER 37 C.F.R. 41.41

Mail Stop AF
Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

INTRODUCTORY REMARKS

This Reply Brief, which is timely, is filed in response to the Examiner's Answer, mailed March 12, 2007.

RECEIVED
CENTRAL FAX CENTER

MAY 11 2007

5136343612

11

PG

03:29:47 p.m.

05-11-2007

3/7

01:54:14 p.m.

05 11 2007

3/7

Appl. No. 09/914,966
Atty. Docket No. 7456R
Reply Brief Dated May 11, 2007
Reply Brief to Examiner's Answer of March 12, 2007
Customer No. 27752

EXAMINER'S ANSWER

The Examiner has acknowledged the correctness of Section 1 through Section 9 of Appellant's Appeal Brief.

This Reply Brief is being filed in view of Section 10, Response to Argument, in the Examiner's Answer.

THE EXAMINER'S POSITION

As stated within the Examiner's Answer, the Examiner continues to maintain that Claims 33-35 and 37-52 are obvious over U.S. Patent No. 4,243,480 to Hernandez et al. ("Hernandez").

The Examiner asserts that Hernandez's disclosed process for making fibers; namely, introducing a starch dispersion into a coagulation bath is capable of making 10 μ m diameter starch fibers. In addition, the Examiner has maintained that Hernandez suggests to one of ordinary skill in the art a starch fiber diameter of less than 10 μ m (e.g., 9.9 μ m). Answer, p. 9. The Examiner further asserts that Hernandez is presumed enabled for a starch fiber having a diameter of 10 μ m since there is no evidence on record establishing otherwise.

The Examiner also continues to maintain that Claim 36 is obvious over Hernandez in view of U.S. Patent No. 5,516,815 to Buehler et al. ("Buehler").

APPELLANT'S REPLY

Appellant respectfully submits that obviousness is established "if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. 35 U.S.C. §103(a) [Emphasis added].

Appellant submits that one of ordinary skill in the art at the time of the invention (March 7, 2000) would not have been taught by Hernandez, alone or with his/her own knowledge and/or other prior art references, how to make 10 μ m diameter starch fibers.

Appl. No. 09/914,966
Atty. Docket No. 7456R
Reply Brief Dated May 11, 2007
Reply Brief to Examiner's Answer of March 12, 2007
Customer No. 27752

Under the current state of the law for obviousness, if a person of ordinary skill in the art can implement a predictable variation, and would see a benefit of doing so, §103 likely bars patentability. *KSR INT'L CO. v. TELEFLEX INC.*, 550 U.S. ____ (2007).

Appellant respectfully submits that a person of ordinary skill in the art could not implement a predictable variation by using his/her own knowledge and the teachings of Hernandez to produce a starch fiber having a fiber diameter of less than 10µm for the following reasons.

First, Appellant respectfully submits that, at the time of the invention, one of ordinary skill in the art would not have had the equipment to make 10µm diameter starch fibers, let alone less than 10µm diameter starch fibers. The state of the art for spinnerette hole diameters, at the time of the invention, was well above 10µm diameter holes. Hernandez teaches in Example 1 a spinnerette having apertures that exhibit a diameter of 70.2µm. This was likely the cutting edge of spinnerette aperture diameters. With the introduction of laser, EDM and E-beam technologies and the application of those to creating holes, especially capillary holes suitable for spinning fibers, the production of spinnerettes with hole diameters of less than 50µm has become commercially feasible. However, one manufacturer that specializes in drilling holes in materials (not necessarily spinnerette materials), National Jet Company (www.najet.com), highlights on their website that they can still only drill holes down to 0.0005 inches (about 13µm). Nowhere is it mentioned or taught on their website that they or any manufacturer can produce a spinnerette for spinning fibers having hole diameters of 10µm or less. Therefore, Appellant submits that, at the time of the invention, spinnerettes for use with Hernandez's process were not commercially available or known to make 10µm or less diameter starch fibers. Therefore, Appellant respectfully submits that Hernandez's process, at the time of the invention, could not have made 10µm or less diameter starch fibers.

Second, even if a spinnerette having a hole diameter of 10µm was available in the art at the time of the invention, Appellant submits that the Mackey Declaration under 37 CFR §1.132 filed December 7, 2005, Section 3 supports the fact that 10µm or less diameter starch fibers could not be produced via such a 10µm diameter hole due to clogging of the hole by particles present within Hernandez's starch dispersion.

Appl. No. 09/914,966
Atty. Docket No. 7456R
Reply Brief Dated May 11, 2007
Reply Brief to Examiner's Answer of March 12, 2007
Customer No. 27752

Third, if one of ordinary skill in the art used a spinnerette having a hole diameter greater than 10 μ m, such as 70.2 μ m diameter hole, like Hernandez's Example 1, there is absolutely no teaching of drawing or attenuating a starch fiber produced from such spinnerette to create a starch fiber having a diameter of less than 10 μ m. Recall that Hernandez introduces its starch dispersion into a coagulating bath where the starch fiber is precipitated almost immediately upon contacting the coagulating bath, thus not permitting an opportunity to significantly draw and/or attenuate the fiber to significantly reduce its fiber diameter, especially to less than 10 μ m.

Fourth, with respect to the Examiner's reliance on the statement, "It is well known that the diameter of a spun fiber is essentially equivalent to the diameter of the extrusion die through which the spun fiber is formed unless the spun fiber is subjected to extremely high attenuation forces." (Mackey Declaration), to assert that Appellant recognizes that it is well known in the art to attenuate fibers, Appellant submits that if 10 μ m diameter hole spinnerettes are not known in the art at the time of the invention, then 10 μ m or less diameter fibers, especially starch fibers, cannot be produced without significant attenuation and Hernandez clearly fails to teach any such attenuation. Appellant submits that combining extremely high attenuation forces to the fiber produced by Hernandez's process is inoperable due to the fact that Hernandez's process teaches introducing its starch dispersion into a coagulation bath, where the fiber is formed, not into air like meltblowing and/or spunbonding fiber spinning processes.

In light of the foregoing reasons, Appellant respectfully submits that Claims 33 and 52 are not rendered obvious over Hernandez. Further, Appellant submits that Claims 34-35 and 37-51, which ultimately depend from Claim 33, are not rendered obvious over Hernandez. MPEP 2143.03.

Further, Appellant respectfully submits that Claim 36, which ultimately depends from Claim 33, discussed above, is not rendered obvious over Hernandez in view of U.S. Patent No. 5,516,815 to Buehler et al. for the same reasons that Claim 33 is not rendered obvious over Hernandez.

Appl. No. 09/914,966
Atty. Docket No. 7456R
Reply Brief Dated May 11, 2007
Reply Brief to Examiner's Answer of March 12, 2007
Customer No. 27752

The remarks contained within this Reply Brief are an addition to the remarks contained within Appellant's Appeal Brief, Amendments and Responses contained in the present Application, which are incorporated herein by reference.

In light of the foregoing, Appellant respectfully requests the Board to reverse all of the rejections by the Examiner in the final rejection, as discussed above.

Respectfully submitted,

THE PROCTER & GAMBLE COMPANY

By 

C. Brant Cook

Attorney for Appellant

Registration No. 39,151

(513) 634-1533

Date: May 11, 2007

Customer No. 27752

RECEIVED
CENTRAL FAX CENTER

03:30:36 p.m. 05-11-2007
01:55:00 p.m. 05 11 2007

7/7
7/7

MAY 11 2007

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No. : 09/914,966
Inventor(s) : Larry Neil Mackey, et al.
Filed : September 6, 2001
Art Unit : 1771
Examiner : Cheryl Ann Juska
Docket No. : 7456R
Confirmation No. : 6640
Customer No. : 27752
Title : ABSORBENT FLEXIBLE STRUCTURE COMPRISING
STARCH FIBERS

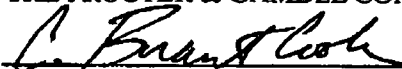
REQUEST FOR ORAL HEARING BEFORE
THE BOARD OF PATENT APPEALS AND INTERFERENCES

Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

An Oral Hearing is hereby requested before the Board of Patent Appeals and Interferences in the appeal of the above-identified application.

Authorization is hereby given to charge the fee required under 37 CFR 41.20(b)(3) or any additional fees that may be required, or credit any overpayment, to Deposit Account No. 16-2480 in the name of The Procter & Gamble Company.

Respectfully submitted,
THE PROCTER & GAMBLE COMPANY

By 
Signature
C. Brant Cook

Date: May 11, 2007
Customer No. 27752
(Appeal - Request for Oral Hearing.doc)
(Last Revised 04/25/2006)

Typed or Printed Name
Registration No. 39,151
(513) 634-1533



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
09/914,966	09/06/2001	Larry Neil Mackey	U 013595-2	6640

27752 7590 03/12/2007
THE PROCTER & GAMBLE COMPANY
INTELLECTUAL PROPERTY DIVISION
WINTON HILL BUSINESS CENTER - BOX 161
6110 CENTER HILL AVENUE
CINCINNATI, OH 45224

EXAMINER

JUSKA, CHERYL ANN

ART UNIT	PAPER NUMBER
----------	--------------

1771

SHORTENED STATUTORY PERIOD OF RESPONSE	MAIL DATE	DELIVERY MODE
2 MONTHS	03/12/2007	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

If NO period for reply is specified above, the maximum statutory period will apply and will expire 6 MONTHS from the mailing date of this communication.



UNITED STATES PATENT AND TRADEMARK OFFICE

Commissioner for Patents
United States Patent and Trademark Office
P.O. Box 1450
Alexandria, VA 22313-1450
www.uspto.gov

**BEFORE THE BOARD OF PATENT APPEALS
AND INTERFERENCES**

Application Number: 09/914,966
Filing Date: September 06, 2001
Appellant(s): MACKEY ET AL.

**MAILED
MAR 12 2007
GROUP 1700**

C. Brant Cook
For Appellant

EXAMINER'S ANSWER

This is in response to the appeal brief filed October 6, 2006, appealing from the Office action mailed February 9, 2006.

(1) Real Party in Interest

A statement identifying by name the real party in interest is contained in the Brief.

(2) Related Appeals and Interferences

The examiner is not aware of any related appeals, interferences, or judicial proceedings which will directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal.

(3) Status of Claims

The statement of the status of claims contained in the Brief is correct.

(4) Status of Amendments After Final

The appellant's statement of the status of amendments after final rejection contained in the Brief is correct.

(5) Summary of Claimed Subject Matter

The summary of claimed subject matter contained in the Brief is correct.

(6) Grounds of Rejection to be Reviewed on Appeal

The appellant's statement of the grounds of rejection to be reviewed on appeal is correct.

(7) Claims Appendix

The copy of the appealed claims contained in the Appendix to the Brief is correct.

(8) Evidence Relied Upon

US 4,243,480	Hernandez et al.	01/1981
US 5,516,815	Buehler et al.	05/1996

(9) Grounds of Rejection

The following ground(s) of rejection are applicable to the appealed claims:

A. Claims 33-35 and 37-52 stand rejected under 35 USC 103(a) as being unpatentable over US 4,243,480 issued to Hernandez et al.

Hernandez teaches starch fibers suited for replacing pulp fibers in making paper (abstract). The fibers have diameters in the range of 10-500 microns (col. 7, lines 7-11) and contain 50% by weight or more of starch (claim 1, col. 21, lines 65-67). The starch fiber may include additives such as a plasticizer and a cross-linking agent in amounts of less than 50% by weight of the total solids (col. 9, lines 22-67). Said cross-linking agent may be urea-formaldehyde, glyoxal, or urea-melamine-formaldehyde resins (col. 9, lines 51-58). The starch fibers can be made into a paper product having a basis weight within the range presently claimed (Tables I, II, V, and XI).

Thus, Hernandez teaches the invention of claims 33-35, 37-41, 48, and 52 with the exception of the average fiber diameter less than 10 microns. As noted above, Hernandez teaches a starch fiber diameter of 10-500 microns rather than the presently claimed less than 10

microns. However, it is argued that the claims are obvious over the teachings of Hernandez. Specifically, it has been held that discovering an optimum value of a result effective variable involves only routine skill in the art. *In re Boesch*, 205 USPQ 215. In the instant case, decreasing the fiber diameter will produce a softer, more absorbent product. Additionally, while the smallest fiber diameter disclosed by Hernandez is 10 microns, this disclosure would have suggested less than 10 microns, such as 9.9 microns based on the reasonable expectation that the suggested value is so close to the disclosed value that the same desirable properties would be expected in either case. See *Titanium Metals Corp. v. Banner*, 227 USPQ 773. Therefore, claims 33-35, 37-41, 48, and 52 are rejected as being obvious over the cited Hernandez reference.

With respect to claims 42-47, Hernandez does not explicitly teach the claimed properties of the fibrous structure (i.e., absorbency, flexibility, and dry and wet tensile strength). However, it is reasonable to presume the claimed properties would be met by the paper product of Hernandez when modified with a fiber diameter less than 10 microns. Support for said presumption is found in the use of like materials (i.e., starch fiber with plasticizer and cross-linking agent or like diameter) and the use of like processes (i.e., forming a paper product having a like basis weight). Like materials cannot have mutually exclusive properties. Therefore, claims 42-47 are rejected also.

With respect to claim 49, Hernandez does not explicitly teach an apparent density of the paper products. However, it would have been obvious to one skilled in the art to produce a fibrous structure according to the Hernandez invention with a fiber diameter of less than 10 microns and having the presently claimed density since it has been held that where the general

Art Unit: 1771

conditions of a claim are disclosed in the prior art, discovering the optimum or workable ranges involves only routine skill in the art. *In re Aller*, 105 USPQ 233. One skilled in the art would readily understand suitable apparent densities for successful paper products. Therefore, claim 49 is also rejected.

Claims 50 and 51 are drawn to the fiber of claim 33 wherein said fiber is a melt blown fiber and a spunbond fiber, respectively. Although Hernandez teaches fiber formation via wet spinning, said claims are rejected as being obvious over the reference. [Note appellant describes Hernandez's process as "solvent spinning."] Specifically, the limitations of claims 50 and 51 amount to method limitations in an article claim. As such, said limitations are only given weight to the extent that said limitations produce a structurally different product. It is believed that the claimed melt spun fibers (i.e., melt blown and spunbond fibers) are not materially different than the solvent spun fibers of Hernandez. Note applicant is not claiming a melt blown or spunbond nonwoven or fibrous structure but rather applicant is merely claiming an individual fiber. There is nothing on record establishing any chemical or structural differences between a fiber that is melt spun versus one that is solvent spun. Therefore, claims 50 and 51 are rejected as being obvious over the cited prior art.

B. Claim 36 stands rejected under 35 USC 103(a) as being unpatentable over the cited Hernandez reference in view of US 5,516,815 issued to Buehler et al.

Hernandez teaches the addition of a plasticizer to the starch fiber, but fails to explicitly teach suitable plasticizers. As such, one must look to the prior art to select a suitable plasticizer. For example, Buehler teaches a starch fiber having a plasticizer such as sorbitol, mannitol, ethylene glycol, and polyethylene glycol. Thus, it would have been obvious to one skilled in the

Art Unit: 1771

art to employ the claimed plasticizers since Hernandez's lack of a teaching to suitable plasticizers must lead one to other prior art, such as Buehler. It has been held to be within the general skill of a worker in the art to select a known material on the basis of its suitability for the intended use. *In re Leshin*, 125 USPQ 416. Therefore, claim 36 is rejected as being obvious over the cited prior art.

(10) Response to Argument

Appellant traverses the rejection of the claims as being obvious over Hernandez by asserting that the reference "fails to teach each and every element of Claim 33" (Brief, page 3, 3rd paragraph). The examiner agrees. As such, the rejection over Hernandez is not a 102 anticipation rejection, but rather a 103 obviousness rejection. Specifically, while Hernandez fails to explicitly teach a fiber diameter of less than 10 microns, the reference does suggest to one of ordinary skill in the art to employ a fiber diameter of less than 10 microns. As noted above, a disclosure of 10 microns suggests less than 10 microns, such as 9.99 microns based on the reasonable expectation that the suggested value is so close to the disclosed value that the same desirable properties would be expected in either case. See *Titanium Metals Corp. v. Banner*, 227 USPQ 773.

Appellant also argues the above rejection by asserting that one of ordinary skill in the art could not produce fibers having an average diameter of less than 10 microns (Brief, paragraph spanning pages 3-4). In particular, appellant asserts that the wet spinning process disclosed by Hernandez could not produce such fine fiber diameters without some form of attenuation or drawing of said fiber (Brief, paragraph spanning pages 3-4). Note the working example of

Art Unit: 1771

Hernandez only teaches a fiber diameter of 65 microns. Since Hernandez is silent with respect to said attenuation or drawing processes, appellant believes the reference fails to enable one of ordinary skill in the art to make fibers of less than 10 microns (Brief, paragraph spanning pages 3-4). Appellant relies upon the Mackey Declaration under 37 CFR 1.132, originally filed December 7, 2005, section 3, as support for this argument.

The examiner respectfully disagrees. First, the reference is not limited to its working examples. “The use of patents as references is not limited to what the patentees describe as their own inventions or to the problems with which they are concerned. They are part of the literature of the art, relevant for all they contain.” *In re Heck*, 216 USPQ 1038, (quoting *In re Lemelson*, 158 USPQ 275). Disclosed examples and preferred embodiments do not constitute a teaching away from a broader disclosure or nonpreferred embodiments. *In re Susi*, 169 USPQ 423. Note the reference *explicitly* teaches diameters ranging from 10 to 500 microns (col. 3, lines 58-64 and claim 1).

Secondly, Hernandez lack of a teaching to attenuation or drawing of the fibers is not sufficient support for establishing the reference is non-enabled for diameters of 10 microns. A reference contains an “enabling disclosure” if the public was in possession of the claimed invention before the date of invention. “Such possession is effected if one of ordinary skill in the art could have combined the publication’s description of the invention with his [or her] own knowledge to make the claimed invention.” *In re Donohue*, 226 USPQ 619. Appellant has not provided evidence showing that a process for making fibers as disclosed by Hernandez was not known at the time of the invention. In fact, appellant asserts the contrary in the Mackey Declaration, section 3, 4th paragraph: “It is well known that the diameter of a spun fiber is

essentially equivalent to the diameter of the extrusion die through which the spun fiber is formed unless the spun fiber is subjected to extremely high attenuation forces.” Hence, appellant’s own declaration establishes that it is well known in the art to attenuate fibers in order to obtain finer diameters. Thus, appellant’s argument that the Hernandez reference is not enabled for the disclosed teaching of 10 microns is found unpersuasive.

Appellant also traverses the present rejection by asserting the starch fibers of the present invention are made by a process (i.e., melt spinning) different from that disclosed by Hernandez (i.e., wet spinning) (Brief, page 4, 1st paragraph). In response, appellant is not claiming a process of making a product, and with the exception of claims 50 and 51, does not even recite any process limitations (i.e., product-by-process claims). Hence, appellant’s argument is found unpersuasive with respect to claims 33-49 and 52.

With respect to claims 50 and 51, as noted above, the method limitations are not given patentable weight at this time since there is nothing on record establishing that said methods produce structurally or chemically different fibers than the prior art fibers produced by a different method. Note appellant’s mere allegations that “it is clear that fibers produced by Hernandez’s wet-spinning process are different than those produced by Appellant’s dry, melt spinning process” or “dry, spunbond process” are insufficient to establish the processes produce different products (Brief, page 4, 3rd paragraph and page 5, 1st paragraph). Therefore, appellant’s argument is also found unpersuasive with respect to claims 50 and 51.

Regarding claim 52, appellant traverses the rejection by asserting that Hernandez “fails to teach each and every element of Claim 52” (Brief, page 5, 2nd paragraph). Again, the rejection over Hernandez is not a 102 anticipation rejection, but rather a 103 obviousness rejection.

Specifically, while Hernandez fails to explicitly teach a fibrous paper product comprising a fiber diameter of less than 10 microns, the reference does suggest to one of ordinary skill in the art to employ a fiber diameter of less than 10 microns. To reiterate, a disclosure of 10 microns suggests less than 10 microns, such as 9.9 microns based on the reasonable expectation that the suggested value is so close to the disclosed value that the same desirable properties would be expected in either case. See *Titanium Metals Corp. v. Banner*, 227 USPQ 773.

Regarding the rejection of claim 36 over Hernandez in view of Buehler, appellant merely argues that Buehler fails to overcome the deficiencies of Hernandez, wherein the reference fails to teach a fiber diameter of less than 10 microns (Brief, paragraph spanning pages 5-6). As explained above, the Hernandez reference is not deficient in suggesting to one of ordinary skill in the art a starch fiber having an average fiber diameter of less than 10 microns. Therefore, appellant's argument is found unpersuasive and the rejection of claim 36 over Hernandez in view of Buehler is maintained.

To summarize, the rejection of claims 33-52 stands over the cited Hernandez reference since said reference explicitly teaches a starch fiber diameter of 10 microns, which readily suggests to one of ordinary skill in the art a starch fiber diameter of less than 10 microns (e.g., 9.9 microns). Additionally, the Hernandez reference is presumed enabled for a starch fiber having a diameter of 10 microns since there is no evidence on record establishing otherwise. Also, appellant has not established that the method limitations of claims 50 and 51 produce structurally or chemically different fibers than those made by the process of the prior art. Furthermore, it is noted that appellant has not presented any evidence of unexpected results obtained from the claimed fiber diameter. It is well settled that where patentability is predicated

Art Unit: 1771

upon a change in a condition of a prior art composition, such as change in size, concentration or the like, the burden is on the applicant to establish with objective evidence that the change is critical, i.e., it leads to a new, unexpected result. *In re Woodruff*, 16 USPQ2d 1934; *In re Aller*, 105 USPQ 233. In the present case, appellant has not attached any criticality to the claimed fiber diameter of less than 10 microns and the disclosed preference for an average fiber diameter “of less than 50 microns, preferably less than 25 microns, more preferably less than 15 microns, even more preferably less than 10 microns, and most preferably less than 5 microns” would seem to allay any suggestion of criticality (see page 24 of specification, lines 10-14).

(11) Related Proceeding(s) Appendix

No decision rendered by a court or the Board is identified by the examiner in the Related Appeals and Interferences section of this examiner’s answer.

For the above reasons, it is believed that the rejections should be sustained.

Respectfully submitted,


Cheryl Juska

Conferees: 
Terrel Morris
Carol Chaney 

FEE TRANSMITTAL for FY 2006 Patent fees are subject to annual revision. Effective December 8, 2004	Complete if Known	
	Application Number	09/914,966
	Confirmation Number	6640
	Filing Date	September 6, 2001
	First Named Inventor	Larry Neil Mackey
	Examiner Name	Cheryl Ann Juska
	Art Unit	1771
TOTAL AMOUNT OF PAYMENT (\$500)		Docket No. 7456R

RECEIVED
CENTRAL FAX CENTER
OCT 06 2006

METHOD OF PAYMENT		FEE CALCULATION (continued)																																					
1. <input checked="" type="checkbox"/> The Director is hereby authorized to charge indicated fees submitted on this form, credit any over payments, and charge any additional fee(s) during the pendency of this application to: Deposit Account Number: 16-2480 Deposit Account Name: The Procter & Gamble Company		5. ADDITIONAL FEES <table border="1"> <thead> <tr> <th>Fee Description</th> <th>Fee Paid</th> </tr> </thead> <tbody> <tr> <td>Extension for reply within 1st month</td> <td>(\$120) <input type="checkbox"/></td> </tr> <tr> <td>Extension for reply within 2nd month</td> <td>(\$450) <input type="checkbox"/></td> </tr> <tr> <td>Extension for reply within 3rd month</td> <td>(\$1,020) <input type="checkbox"/></td> </tr> <tr> <td>Extension for reply within 4th month</td> <td>(\$1,590) <input type="checkbox"/></td> </tr> <tr> <td>Extension for reply within 5th month</td> <td>(\$2,160) <input type="checkbox"/></td> </tr> <tr> <td>Information Disclosure Statement fee</td> <td>(\$180) <input type="checkbox"/></td> </tr> <tr> <td>37 CFR 1.16(f) Late Oath/Declaration (nonprovisional)</td> <td>(\$130) <input type="checkbox"/></td> </tr> <tr> <td>37 CFR 1.17 (q) Surcharge - Late provisional filing fee or cover sheet</td> <td>(\$50) <input type="checkbox"/></td> </tr> <tr> <td>Non-English specification</td> <td>(\$130) <input type="checkbox"/></td> </tr> <tr> <td>Notice of Appeal</td> <td>(\$500) <input type="checkbox"/></td> </tr> <tr> <td>Filing a brief in support of an appeal</td> <td>(\$500) <input checked="" type="checkbox"/></td> </tr> <tr> <td>Request for oral hearing</td> <td>(\$1,000) <input type="checkbox"/></td> </tr> <tr> <td>Acceptance of unintentionally delayed claim for priority under 35 U.S.C. 119, 120, 121, or 365 (a) or (c)</td> <td>(\$1,370) <input type="checkbox"/></td> </tr> <tr> <td>Other:</td> <td><input type="checkbox"/></td> </tr> </tbody> </table>		Fee Description	Fee Paid	Extension for reply within 1 st month	(\$120) <input type="checkbox"/>	Extension for reply within 2 nd month	(\$450) <input type="checkbox"/>	Extension for reply within 3 rd month	(\$1,020) <input type="checkbox"/>	Extension for reply within 4 th month	(\$1,590) <input type="checkbox"/>	Extension for reply within 5 th month	(\$2,160) <input type="checkbox"/>	Information Disclosure Statement fee	(\$180) <input type="checkbox"/>	37 CFR 1.16(f) Late Oath/Declaration (nonprovisional)	(\$130) <input type="checkbox"/>	37 CFR 1.17 (q) Surcharge - Late provisional filing fee or cover sheet	(\$50) <input type="checkbox"/>	Non-English specification	(\$130) <input type="checkbox"/>	Notice of Appeal	(\$500) <input type="checkbox"/>	Filing a brief in support of an appeal	(\$500) <input checked="" type="checkbox"/>	Request for oral hearing	(\$1,000) <input type="checkbox"/>	Acceptance of unintentionally delayed claim for priority under 35 U.S.C. 119, 120, 121, or 365 (a) or (c)	(\$1,370) <input type="checkbox"/>	Other:	<input type="checkbox"/>						
Fee Description	Fee Paid																																						
Extension for reply within 1 st month	(\$120) <input type="checkbox"/>																																						
Extension for reply within 2 nd month	(\$450) <input type="checkbox"/>																																						
Extension for reply within 3 rd month	(\$1,020) <input type="checkbox"/>																																						
Extension for reply within 4 th month	(\$1,590) <input type="checkbox"/>																																						
Extension for reply within 5 th month	(\$2,160) <input type="checkbox"/>																																						
Information Disclosure Statement fee	(\$180) <input type="checkbox"/>																																						
37 CFR 1.16(f) Late Oath/Declaration (nonprovisional)	(\$130) <input type="checkbox"/>																																						
37 CFR 1.17 (q) Surcharge - Late provisional filing fee or cover sheet	(\$50) <input type="checkbox"/>																																						
Non-English specification	(\$130) <input type="checkbox"/>																																						
Notice of Appeal	(\$500) <input type="checkbox"/>																																						
Filing a brief in support of an appeal	(\$500) <input checked="" type="checkbox"/>																																						
Request for oral hearing	(\$1,000) <input type="checkbox"/>																																						
Acceptance of unintentionally delayed claim for priority under 35 U.S.C. 119, 120, 121, or 365 (a) or (c)	(\$1,370) <input type="checkbox"/>																																						
Other:	<input type="checkbox"/>																																						
FEE CALCULATION 2. BASIC FILING FEE - Large Entity <table border="1"> <thead> <tr> <th>FILING FEE</th> <th>SEARCH FEE</th> <th>EXAMINATION FEE</th> <th>Fee Paid</th> </tr> </thead> <tbody> <tr> <td>Application Type</td> <td></td> <td></td> <td></td> </tr> <tr> <td>Nonprovisional (\$300)</td> <td>(\$500)</td> <td>(\$200)</td> <td></td> </tr> <tr> <td>Utility</td> <td></td> <td>(Total = \$1000)</td> <td><input type="checkbox"/></td> </tr> <tr> <td>Design (\$200)</td> <td>(\$100)</td> <td>(\$130)</td> <td></td> </tr> <tr> <td></td> <td></td> <td>(Total = \$430)</td> <td><input type="checkbox"/></td> </tr> <tr> <td>Reissue (\$300)</td> <td>(\$500)</td> <td>(\$600)</td> <td></td> </tr> <tr> <td></td> <td></td> <td>(Total = \$1400)</td> <td><input type="checkbox"/></td> </tr> <tr> <td>Provisional Utility filing fee</td> <td></td> <td>(Total = \$200)</td> <td><input type="checkbox"/></td> </tr> </tbody> </table>		FILING FEE	SEARCH FEE	EXAMINATION FEE	Fee Paid	Application Type				Nonprovisional (\$300)	(\$500)	(\$200)		Utility		(Total = \$1000)	<input type="checkbox"/>	Design (\$200)	(\$100)	(\$130)				(Total = \$430)	<input type="checkbox"/>	Reissue (\$300)	(\$500)	(\$600)				(Total = \$1400)	<input type="checkbox"/>	Provisional Utility filing fee		(Total = \$200)	<input type="checkbox"/>		
FILING FEE	SEARCH FEE	EXAMINATION FEE	Fee Paid																																				
Application Type																																							
Nonprovisional (\$300)	(\$500)	(\$200)																																					
Utility		(Total = \$1000)	<input type="checkbox"/>																																				
Design (\$200)	(\$100)	(\$130)																																					
		(Total = \$430)	<input type="checkbox"/>																																				
Reissue (\$300)	(\$500)	(\$600)																																					
		(Total = \$1400)	<input type="checkbox"/>																																				
Provisional Utility filing fee		(Total = \$200)	<input type="checkbox"/>																																				
3. APPLICATION SIZE FEE: Sheets of Spec and Drawings <input type="checkbox"/> (\$250 for each 50 sheets in excess of 100, except for sequence and program listings) SUBTOTAL (2)+(3) (\$) <input type="checkbox"/>																																							
4. EXTRA CLAIM FEES FOR UTILITY AND REISSUE: <table border="1"> <thead> <tr> <th></th> <th>Extra Claims</th> <th>Fee from Below</th> <th>Fee Paid</th> </tr> </thead> <tbody> <tr> <td>Total Claims</td> <td><input type="checkbox"/> - 20** = <input type="checkbox"/> x</td> <td><input type="checkbox"/> =</td> <td><input type="checkbox"/></td> </tr> <tr> <td>Independent Claims</td> <td><input type="checkbox"/> - 3** = <input type="checkbox"/> x</td> <td><input type="checkbox"/> =</td> <td><input type="checkbox"/></td> </tr> <tr> <td>Multiple Dependent claims:</td> <td></td> <td><input type="checkbox"/> =</td> <td><input type="checkbox"/></td> </tr> </tbody> </table> ** or number previously paid, if greater. For Reissues, see below Fee Description Claims in excess of 20 (\$50 per claim) Independent claims in excess of 3 (\$200 per claim) Multiple dependent claim, if not paid (\$360) **Reissue: each independent claim over 3 and more than in the original patent (\$200 per claim) **Reissue claims: each claim over 20 and more than original patent (\$50 per claim) SUBTOTAL (4) (\$) <input type="checkbox"/>			Extra Claims	Fee from Below	Fee Paid	Total Claims	<input type="checkbox"/> - 20** = <input type="checkbox"/> x	<input type="checkbox"/> =	<input type="checkbox"/>	Independent Claims	<input type="checkbox"/> - 3** = <input type="checkbox"/> x	<input type="checkbox"/> =	<input type="checkbox"/>	Multiple Dependent claims:		<input type="checkbox"/> =	<input type="checkbox"/>	SUBTOTAL(5) (\$) [500]																					
	Extra Claims	Fee from Below	Fee Paid																																				
Total Claims	<input type="checkbox"/> - 20** = <input type="checkbox"/> x	<input type="checkbox"/> =	<input type="checkbox"/>																																				
Independent Claims	<input type="checkbox"/> - 3** = <input type="checkbox"/> x	<input type="checkbox"/> =	<input type="checkbox"/>																																				
Multiple Dependent claims:		<input type="checkbox"/> =	<input type="checkbox"/>																																				

SUBMITTED BY		Complete (if applicable)	
Name (Print/Type)	C. Brant Cook	Registration No. (Attorney/Agent)	39,151
Signature	<i>C. Brant Cook</i>	Telephone	(513) 634-1533
		Date	October 6, 2006

+ This collection of information is required by 37 CFR 1.17. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon individual case. Any comments on the amount of time you are required to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P. O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

Fee Transmittal Doc (Revised for P&G use 04/23/2006)

OCT 06 2006

IMPORTANT CONFIDENTIALITY NOTICE

The documents accompanying this telecopy transmission contain confidential information belonging to the sender which is legally protected. The information is intended only for the use of the individual or entity named below. If you are not the intended recipient, you are hereby notified that any disclosure, copying, distribution or the taking of any action in reliance on the contents of this telecopied information is strictly prohibited. If you have received this telecopy in error, please immediately notify us by telephone (collect) to arrange for return of the telecopied document to us.

TO: MAIL STOP APPEAL BRIEF - PATENTS - United States Patent and Trademark Office
EXAMINER CHERYL ANN JUSKA

Fax No. 571-273-8300

Phone No.

FROM: Connie Baker (Typed or printed name of person signing Certificate)

Fax No. 513-634-6312

Phone No. 513-634-0567

Application No.: 09/914,966

Inventor(s): Larry Neil Mackey, et al.

Filed: September 6, 2006

Docket No.: 7456R

Confirmation No.: 6640

FACSIMILE TRANSMITTAL SHEET AND
CERTIFICATE OF TRANSMISSION UNDER 37 C.F.R. §1.8

I hereby certify that this correspondence is being facsimile transmitted to the United States Patent and Trademark Office on October 6, 2006, to the above-identified facsimile number.

Connie Baker (Signature)

Listed below are the item(s) being submitted with this Certificate of Transmission:**

- 1) Fee Transmittal
- 2) Appeal Brief (14 pages)
- 3)
- 4)

Number of Pages Including this Page: 16

Comments:

****Note:** Each paper must have its own certificate of transmission, OR this certificate must identify each submitted paper.

**RECEIVED
CENTRAL FAX CENTER****OCT 06 2006****IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Application No. : 09/914,966
Applicant(s) : LARRY NEIL MACKEY et al.
Filed : September 6, 2001
Title : ABSORBENT FLEXIBLE STRUCTURE
: COMPRISING STARCH FIBERS
TC/A.U. : 1771
Examiner : Cheryl Ann Juska
Conf. No. : 6640
Docket No. : 7456R
Customer No. : 27752

APPEAL BRIEF

Mail Stop Appeal Brief - Patents

Commissioner for Patents

P. O. Box 1450

Alexandria, VA 22313-1450

Dear Sir,

This Brief is filed pursuant to the appeal from the U.S. Patent and Trademark Office decision of the Final Office Action mailed February 9, 2006. A timely Notice of Appeal was filed on April 25, 2006.

REAL PARTY IN INTEREST

The real party of interest is The Procter & Gamble Company of Cincinnati, Ohio.

RELATED APPEALS AND INTERFERENCES

There are no known related appeals, interferences, or judicial proceedings.

STATUS OF CLAIMS

Claims 1-32 are cancelled.

Claims 33 to 52 are rejected.

Claims 33 to 52 are appealed.

10/10/2006 EFLORES 00000021 162480 09914966

01 FC:1402 500.00 DA

Appl. No. 09/914,966
Atty. Docket No. 7456R
Appeal Brief dated October 6, 2006
Reply to Office Action of September 8, 2006
Customer No. 27752

A complete copy of the appealed claims is set forth in the Claims Appendix attached herein.

STATUS OF AMENDMENTS

An Amendment After Final was filed on April 10, 2006. However, the Examiner did not enter the amendment per the Examiner's Advisory Action dated April 14, 2006.

SUMMARY OF CLAIMED SUBJECT MATTER

The present invention relates to fibers comprising starch (Page 5, lines 18-29; Figs. 7A and 7B) ("starch fibers"), wherein the fibers have an average fiber diameter of less than 10 μm (Page 24, lines 10-14), to a fibrous structure (Page 9, lines 15-16) comprising a plurality of such starch fibers and to a paper product (Page 9, lines 10-12) comprising such a fibrous structure (Page 9, lines 15-16).

GROUND'S OF REJECTION TO BE REVIEWED ON APPEAL

Claims 33-35 and 37-52 stand finally rejected under 35 U.S.C. §103(a) over U.S. Patent No. 4,243,480 to Hernandez et al.

- i. Claims 33-35 and 37-49
- ii. Claim 50
- iii. Claim 51
- iv. Claim 52

Claim 36 stands finally rejected under 35 U.S.C. §103(a) over U.S. Patent No. 4,243,480 to Hernandez et al. in view of U.S. Patent No. 5,516,815 to Buehler et al.

- i. Claim 36

ARGUMENTS

Rejection Under 35 U.S.C. §103(a) over U.S. Patent No. 4,243,480 to Hernandez et al.

Claims 33-35 and 37-52 stand finally rejected under 35 U.S.C. §103(a) as defining obvious subject matter over U.S. Patent No. 4,243,480 to Hernandez et al. ("Hernandez"). The Examiner asserts that Hernandez teaches a starch fiber having a diameter of 10 to 500 microns.

Appl. No. 09/914,966
Atty. Docket No. 7456R
Appeal Brief dated October 6, 2006
Reply to Office Action of September 8, 2006
Customer No. 27752

i. Claims 33-35 and 37-49

The Examiner asserts that Hernandez's teaching of starch fibers having a diameter of 10 to 500 microns (Hernandez, Col. 3, lines 58-64) renders Claim 33, an independent claim, and Claims 34-35 and 37-49, which ultimately depend from Claim 33, obvious.

Appellant respectfully submits that Claim 33 claims a fiber comprising starch, wherein the fiber has an average fiber diameter of less than 10 microns. Accordingly, Appellant respectfully disagrees with the Examiner's conclusion of obviousness.

Appellant respectfully submits that Hernandez fails to teach each and every element of Claim 33. Appellant submits that Hernandez teaches only one type of fiber spinning; namely, wet fiber spinning (solvent spun fibers). Hernandez teaches that its fibers are precipitated by extrusion of a thread-like stream of a colloidal dispersion of starch at 5-40%, by weight solids, into a suitable moving coagulating salt solution. (Hernandez, Col. 3, lines 58-64). One of ordinary skill in the art understands that as a result of the fiber spinning process taught by Hernandez, Hernandez's diameters for its fibers are relatively large (i.e., greater than 50 microns). There is no way that one of ordinary skill in the art could take Hernandez's teachings and produce fibers comprising starch, wherein the fibers have an average fiber diameter of less than 10 microns. The smallest average fiber diameter fiber that Hernandez explicitly teaches having made is a 65 micron average fiber diameter fiber. (Hernandez, Col. 12, lines 47-49). Appellant submits that in order to achieve less than 10 micron average fiber diameter fibers, the fibers need to be subjected to a significant force, such as an attenuation air stream (as shown and described in the present invention, Fig. 4), in order to reduce the average fiber diameter of the fiber being produced to less than 10 microns. The wet-spinning process taught by Hernandez does not apply a significant force that is capable of reducing the average fiber diameter of the fiber being produced to less than 10 microns. Hernandez doesn't even teach any process, such as mechanical drawing, that may aid in reducing its fibers' diameters. Hernandez only briefly mentions that the coagulating salt solution that its fibers are being produced in is moving. Therefore, Appellant respectfully submits that due to Hernandez's blatant failure to teach the need for or any process to attenuate (i.e., reduce the fibers' diameters) its fibers, one of ordinary skill in the art could not make fibers comprising starch, wherein the fibers have an average fiber diameter of less than 10

Appl. No. 09/914,966
Atty. Docket No. 7456R
Appeal Brief dated October 6, 2006
Reply to Office Action of September 8, 2006
Customer No. 27752

microns based on Hernandez's teachings. Additional support for Appellant's position is found in the 37 CFR §1.132 Declaration by Larry Neil Mackey, an inventor of the claimed invention, attached hereto in the Evidence Appendix.

In addition to the deficiencies in Hernandez's teachings, Appellant respectfully submits that as described in Appellant's specification, its claimed fibers are made by a completely different process; namely, a dry-spinning process, such as a melt spinning process (Page 33, lines 25-26). Appellant's fibers are produced by extruding a starch composition through an extruder (10 of Fig. 4) to form fibers (12 of Fig. 4). The starch composition, extruded under pressure, is forced through a spinneret forming a vertically oriented curtain of downward advancing fibers (Page 33, lines 28-29; 12 of Fig. 4). The fibers (12 of Fig. 4) are quenched with air in conjunction with a suction-type drawing or attenuating air slot (22 of Fig. 4). The starch composition and the attenuation force described in the present invention facilitates the production of small average fiber diameter fibers (i.e., less than 10 microns).

In light of the foregoing, Appellant respectfully submits that Hernandez fails to teach each and every element of Claim 33 and therefore, fails to render Claim 33 obvious. MPEP 2143.03. At the very most, Hernandez merely teaches that it would have been obvious to try to make less than 10 micron average fiber diameter fiber. Further, Appellant respectfully submits that Claims 34-35 and 37-49, which ultimately depend from Claim 33, are not rendered obvious over Hernandez. MPEP 2143.03.

ii. Claim 50

Appellant respectfully submits that Hernandez fails to teach each and every element of Claim 50, which depends from Claim 33, because Hernandez fails to teach a melt blown fiber comprising starch. As discussed above, Hernandez teaches only one process, a wet-spinning process wherein fibers are precipitated into a coagulating salt solution. Further, Appellant submits that it is clear that fibers produced by Hernandez's wet-spinning process are different than those produced by Appellant's dry, melt spinning process. Further yet, Appellant submits that Claim 50, which depends from Claim 33, is not rendered obvious over Hernandez for the same reasons that Claim 33 is not rendered obvious over Hernandez. MPEP 2143.03.

Appl. No. 09/914,966
Atty. Docket No. 7456R
Appeal Brief dated October 6, 2006
Reply to Office Action of September 8, 2006
Customer No. 27752

iii. Claim 51

Appellant respectfully submits that Hernandez fails to teach each and every element of Claim 51, which depends from Claim 33, because Hernandez fails to teach a spunbond fiber comprising starch. As discussed above, Hernandez teaches only one process, a wet-spinning process wherein fibers are precipitated into a coagulating salt solution. Further, Appellant submits that it is clear that fibers produced by Hernandez's wet-spinning process are different than those produced by Appellant's dry, spunbond process. Further yet, Appellant submits that Claim 51, which depends from Claim 33, is not rendered obvious over Hernandez for the same reasons that Claim 33 is not rendered obvious over Hernandez. MPEP 2143.03.

iv. Claim 52

Appellant respectfully submits that Hernandez fails to teach each and every element of Claim 52, an independent claim, because Hernandez fails to teach a paper product comprising a fibrous structure, wherein the fibrous structure comprises a fiber comprising starch, wherein the fiber has an average fiber diameter of less than 10 microns. For the reasons discussed above, Hernandez fails to teach a starch fiber having an average fiber diameter of less than 10 microns.

Rejection Under 35 U.S.C. §103(a) over U.S. Patent No. 4,243,480 to Hernandez et al. in view of U.S. Patent No. 5,516,815 to Buehler et al.

Claim 36 stands finally rejected under 35 U.S.C. §103(a) as defining obvious subject matter over U.S. Patent No. 4,243,480 to Hernandez et al. ("Hernandez") in view of U.S. Patent No. 5,516,815 to Buehler et al. ("Buehler"). The Examiner asserts that Hernandez teaches the addition of a plasticizer to its starch fiber, but fails to explicitly teach suitable plasticizers. The Examiner asserts that Buehler teaches a starch fiber having a plasticizer such as sorbitol, mannitol, ethylene glycol and polyethylene glycol. The Examiner concludes that it would have been obvious to one skilled in the art to employ the claimed plasticizers since Hernandez's lack of a teaching to suitable plasticizers must lead one to other prior art, such as Buehler.

Appellant respectfully disagrees with the Examiner's conclusion. Appellant respectfully submits that the combined teachings of Hernandez and Buehler fail to teach each and every element of Claim 36. Appellant submits that Hernandez, as discussed

Appl. No. 09/914,966
Atty. Docket No. 7456R
Appeal Brief dated October 6, 2006
Reply to Office Action of September 8, 2006
Customer No. 27752

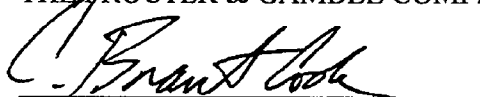
above, fails to teach a fiber comprising starch, wherein the fiber has an average fiber diameter of less than 10 microns. Further, Appellant submits that Buehler fails to overcome the deficiencies of Hernandez since it, like Hernandez, fails to teach a fiber comprising starch, wherein the fiber has an average fiber diameter of less than 10 microns. In addition, Appellant submits that Claim 36, which ultimately depends from Claim 33, is not rendered obvious over the teachings of Hernandez in view of Buehler for the same reasons that Claim 33 is not rendered obvious over the teachings of Hernandez, alone. MPEP 2143.03.

SUMMARY

In view of all of the above, it is respectfully submitted that Claims 33-52 are in condition for allowance.

Respectfully submitted,

THE PROCTER & GAMBLE COMPANY



Signature

C. Brant Cook

Registration No. 39,151

(513) 634-1533

Date: October 6, 2006
Customer No. 27752

Appl. No. 09/914,966
Atty. Docket No. 7456R
Appeal Brief dated October 6, 2006
Reply to Office Action of September 8, 2006
Customer No. 27752

CLAIMS APPENDIX

Claim 33 A fiber comprising starch, wherein the fiber has an average fiber diameter of less than 10 μm .

Claim 34 The fiber according to Claim 33 wherein the fiber comprises from about 20% to about 99.99% by weight of the fiber of starch.

Claim 35 The fiber according to Claim 33 wherein the fiber further comprises a plasticizer.

Claim 36 The fiber according to Claim 35 wherein the plasticizer selected from the group consisting of: sorbitol, monosaccharides, disaccharides, glycerol, polyvinyl alcohol, polyethylene glycol and mixtures thereof.

Claim 37 The fiber according to Claim 35 wherein the plasticizer is present in the fiber at a level of from about 5% to about 70% by weight of the fiber.

Claim 38 The fiber according to Claim 33 wherein the fiber further comprises a cross-linking agent.

Claim 39 The fiber according to Claim 38 wherein the cross-linking agent is selected from the group consisting of: polyamide-epichlorohydrin resins, urea-formaldehyde resins, glyoxylated polyacrylamide resins, melamine formaldehyde resins, polyethylenimine resins, dialdehyde starch resins and mixtures thereof.

Claim 40 The fiber according to Claim 38 wherein the cross-linking agent is present in the fiber at a level of from about 0.1% to about 10% by weight of the fiber.

Claim 41 A fibrous structure comprising a plurality of fibers, wherein at least one fiber is a fiber according to Claim 33.

Appl. No. 09/914,966
Atty. Docket No. 7456R
Appeal Brief dated October 6, 2006
Reply to Office Action of September 8, 2006
Customer No. 27752

Claim 42 The fibrous structure according to Claim 41 wherein the fibrous structure has an absorbency ranging from about $1 \frac{g_{\text{Water}}}{g_{\text{Dry Structure}}}$ to about $15 \frac{g_{\text{Water}}}{g_{\text{Dry Structure}}}$.

Claim 43 The fibrous structure according to Claim 41 wherein the fibrous structure has a total flexibility ranging from about 1.0 g/cm to about 75 g/cm.

Claim 44 The fibrous structure according to Claim 41 wherein the fibrous structure has a geometric mean dry tensile strength ranging from about 10 g/cm to about 1200 g/cm.

Claim 45 The fibrous structure according to Claim 41 wherein the fibrous structure has an initial geometric mean wet tensile strength ranging from about 2 g/cm to about 400 g/cm.

Claim 46 The fibrous structure according to Claim 45 wherein the fibrous structure has an initial geometric mean wet tensile strength ranging from about 2 g/cm to about 200 g/cm.

Claim 47 The fibrous structure according to Claim 41 wherein the fibrous structure has a geometric mean decayed wet tensile strength ranging from about 0 g/cm to about 20 g/cm.

Claim 48 The fibrous structure according to Claim 41 wherein the fibrous structure has a basis weight ranging from about 10 g/m^2 to about 450 g/m^2 .

Claim 49 The fibrous structure according to Claim 41 wherein the fibrous structure has an apparent density ranging from about 0.04 g/cm^3 to about 0.12 g/cm^3 .

Claims 50 The fiber according to Claim 33 wherein the fiber is a melt blown fiber.

Claim 51 The fiber according to Claim 33 wherein the fiber is a spunbond fiber.

Appl. No. 09/914,966
Atty. Docket No. 7456R
Appeal Brief dated October 6, 2006
Reply to Office Action of September 8, 2006
Customer No. 27752

Claim 52 A paper product comprising a fibrous structure, wherein the fibrous structure comprises a fiber comprising starch, wherein the fiber has an average fiber diameter of less than 10 μm .

Appl. No. 09/914,966
Atty. Docket No. 7456R
Appeal Brief dated October 6, 2006
Reply to Office Action of September 8, 2006
Customer No. 27752

EVIDENCE APPENDIX

This Evidence Appendix contains a copy of a 37 CFR §1.132 Declaration that was submitted by the Applicants during prosecution of the appealed application on December 7, 2005 and entry of such Declaration was evidenced in the Examiner's February 9, 2006 Office Action.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No.	: 09/914,966
Applicant(s)	: LARRY NEIL MACKEY et al.
Filed	: September 6, 2001
Title	: ABSORBENT FLEXIBLE STRUCTURE : COMPRISING STARCH FIBERS
TC/A.U.	: 1771
Examiner	: Cheryl Ann Juska
Conf. No.	: 6640
Docket No.	: 7456R
Customer No.	: 27752

DECLARATION UNDER 37 CFR 1.132

Mail Stop RCE
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22213-1450

Dear Sir:

I, Larry Neil Mackey, hereby declare the following:

1. THAT, I am a named-inventor of the above-identified patent application;
2. THAT, I received a Ph.D. in Analytical Chemistry from The Ohio State University in 1975 and have been employed by The Procter & Gamble Company, as a

Appl. No. 09/914,966
Atty. Docket No. 7456R
Appeal Brief dated October 6, 2006
Reply to Office Action of September 8, 2006
Customer No. 27752

Research Fellow assigned primarily to Procter & Gamble's starch fiber project, the subject of the present application, since 1998.

3. I am familiar with U.S. Patent No. 4,243,480 to Hernandez et al. ("Hernandez"). I have thoroughly reviewed Hernandez and it is my technical opinion that Hernandez fails to adequately teach fibers comprising starch, wherein the fibers have an average fiber diameter of less than 10 μm .

As is recognized by the Examiner, Hernandez teaches solvent spun fibers. Further, Hernandez explicitly describes obtaining its fibers via precipitation of a colloidal dispersion of starch in a coagulating salt solution. Hernandez, Col. 2, lines 24-32; Col. 3, lines 58-64.

Hernandez only teaches making one diameter of starch fiber; namely, a fiber having an average fiber diameter of 65 μm . Hernandez, Col. 12, lines 39-49. Nowhere does Hernandez even attempt to teach making a starch fiber having an average fiber diameter of 10 μm . At the very most, Hernandez merely mentions that "the only requirement [of its fibers] being that the waterinsensitive [sic] fibers have a diameter of 10 to 500 microns." Hernandez, Col. 3, lines 59-61. Hernandez never explicitly teaches or enables one of ordinary skill in the art how to make a starch fiber having a fiber diameter of less than 10 μm using its solvent spinning process. In light of the foregoing, at the very most, Hernandez's brief mentioning of "requirements" of its fibers merely suggests to one of ordinary skill in the art to try making a fiber having a fiber diameter of 10 microns. Hernandez provides no reasonable expectation of success that a starch fiber having a fiber diameter of 10 microns can be made by its solvent spinning process.

It is well known that the diameter of a spun fiber is essentially equivalent to the diameter of the extrusion die through which the spun fiber is formed unless the spun fiber is subjected to extremely high attenuation forces. In other words, as is shown in Hernandez's Example 1, a 65 micron diameter fiber is formed by passing a dispersion of starch through 70.2 micron diameter apertures within a die. Accordingly, based on Hernandez's teachings, in order to produce 10 micron diameter fibers, one would have to pass a starch dispersion through about a 10 micron diameter aperture. This is not feasible since starch dispersions typically contain from 3-20 micron granules that would clog a 10 micron diameter aperture.

Appl. No. 09/914,966
Atty. Docket No. 7456R
Appeal Brief dated October 6, 2006
Reply to Office Action of September 8, 2006
Customer No. 27752

As a result, I and my colleagues unexpectedly found that extremely high attenuation forces need to be applied to a spun starch fiber in order to obtain less than 10 micron diameter fibers. In one example we use about a 300 micron diameter extrusion die that would produce about 300 micron diameter fibers UNLESS extremely high attenuation forces are applied to the fiber. Since we subject the fiber to extremely high attenuation forces, our final fiber diameter is less than 10 microns. Hernandez does not teach significantly attenuating its fiber after exiting the die. The final diameter of a spun fiber is related to the elongation needed (attenuation facilitates elongation of the fiber). More particularly, for example, in order to obtain a 10 μm fiber from a starch composition that exits a 70 μm aperture in a die (as described in Hernandez's Example 1), the elongation required is equal to $(70 \mu\text{m})^2 / (10 \mu\text{m})^2$. However, Hernandez fails to mention, even in passing, the need to elongate and/or attenuate its fibers after they exit the die.

I, being one of at least ordinary, if not above ordinary skill in the art of starch fiber spinning, am not able to use the teachings of Hernandez to make a starch fiber having a fiber diameter of 10 microns. Therefore, it is my technical opinion that Hernandez falls well short of adequately describing and teaching how to make a starch fiber having a fiber diameter of 10 microns. Apparently, Hernandez only teaches how to make a starch fiber having an average fiber diameter of 65 microns. Hernandez, Col. 12, Example 1.

4. I am familiar with U.S. Patent No. 5,516,815 to Buehler et al. ("Buehler"). I have thoroughly reviewed Buehler and it is my technical opinion that Buehler fails to remedy the deficiencies associated with Hernandez, discussed above.

5. With regard to the claimed invention of the above-named application, I submit that I and my co-inventors have unexpectedly found that starch fibers having an average diameter of less than 10 μm can be produced via melt spinning and/or spunbond processes so long as significant amounts of attenuation air are applied to the fibers after exiting the dies in order to elongate the fibers to a final average fiber diameter of less than 10 μm . Before our discovery and invention, no one had ever been able to spin starch fibers having an average fiber diameter of less than 10 μm .

Appl. No. 09/914,966
Atty. Docket No. 7456R
Appeal Brief dated October 6, 2006
Reply to Office Action of September 8, 2006
Customer No. 27752

I, Larry Neil Mackey, declare all statements made herein are true to the best of my knowledge, or if made upon information and belief, are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Further Declarant sayeth not.

Larry Neil Mackey
Larry Neil Mackey
Date: 12-07-05

132Declaration.doc

Appl. No. 09/914,966
Atty. Docket No. 7456R
Appeal Brief dated October 6, 2006
Reply to Office Action of September 8, 2006
Customer No. 27752

RELATED PROCEEDINGS APPENDIX

None



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
09/914,966	09/06/2001	Larry Neil Mackey	U 013595-2	6640

27752 7590 02/09/2006

THE PROCTER & GAMBLE COMPANY
INTELLECTUAL PROPERTY DIVISION
WINTON HILL TECHNICAL CENTER - BOX 161
6110 CENTER HILL AVENUE
CINCINNATI, OH 45224

EXAMINER

JUSKA, CHERYL ANN

ART UNIT	PAPER NUMBER
----------	--------------

1771

DATE MAILED: 02/09/2006

Please find below and/or attached an Office communication concerning this application or proceeding.

Office Action Summary	Application No. 09/914,966	Applicant(s) MACKEY ET AL.	
	Examiner Cheryl Juska	Art Unit 1771	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --
Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

- 1) ☒ Responsive to communication(s) filed on 07 December 2005.
- 2a) ☒ This action is **FINAL**. 2b) ☐ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

- 4) ☒ Claim(s) 33-52 is/are pending in the application.
- 4a) Of the above claim(s) _____ is/are withdrawn from consideration.
- 5) ☐ Claim(s) _____ is/are allowed.
- 6) ☒ Claim(s) 33-52 is/are rejected.
- 7) ☐ Claim(s) _____ is/are objected to.
- 8) ☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on _____ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

- 12) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All b) ☐ Some * c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
2. ☐ Certified copies of the priority documents have been received in Application No. _____.
3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).
- * See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

- | | |
|--|---|
| 1) <input type="checkbox"/> Notice of References Cited (PTO-892) | 4) <input type="checkbox"/> Interview Summary (PTO-413)
Paper No(s)/Mail Date. _____ |
| 2) <input type="checkbox"/> Notice of Draftsperson's Patent Drawing Review (PTO-948) | 5) <input type="checkbox"/> Notice of Informal Patent Application (PTO-152) |
| 3) <input type="checkbox"/> Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08)
Paper No(s)/Mail Date _____ | 6) <input type="checkbox"/> Other: _____ |

DETAILED ACTION

Continued Examination Under 37 CFR 1.114

1. A request for continued examination under 37 CFR 1.114, including the fee set forth in 37 CFR 1.17(e), was filed in this application after final rejection. Since this application is eligible for continued examination under 37 CFR 1.114, and the fee set forth in 37 CFR 1.17(e) has been timely paid, the finality of the previous Office action has been withdrawn pursuant to 37 CFR 1.114.

Response to Amendment

2. Applicant's amendment filed December 7, 2005, has been entered. Claims 1-32 are cancelled and replaced with new claims 33-52.

Claim Rejections - 35 USC § 103

3. The text of those sections of Title 35, U.S. Code not included in this action can be found in a prior Office action.

4. Claims 33-35 and 37-52 are rejected under 35 USC 103(a) as being unpatentable over US 4,243,480 issued to Hernandez et al.

New claims 33-35 and 37-52 are of identical scope as that of claims 11-13, 15-29, 31, and 32 as amended in the response filed September 27, 2004. As such, said claims are rejected for the reasons set forth in sections 4, 6, and 7 of the Office Action dated December 10, 2004.

Art Unit: 1771

5. Claim 36 is rejected under 35 USC 103(a) as being unpatentable over the cited Hernandez reference in view of US 5,516,815 issued to Buehler et al.

New claims 36 is of identical scope as that of claim 14 as amended in the response filed September 27, 2004. As such, said claim is rejected for the reasons set forth in section 5 of the Office Action dated December 10, 2004.

Response to Arguments

6. Applicant's arguments filed with the amendment of December 7, 2005, have been fully considered but they are not persuasive.

7. Applicant traverses the above rejections by asserting that the claimed invention is "not rendered obvious over Hernandez because Hernandez fails to teach each and every element of the claims (Remarks, page 1, 9th paragraph). In response, the examiner agrees that Hernandez does not teach "each and every element" of the claimed invention. As such, the rejection is not a 102 anticipation rejection, but rather a 103 rejection. However, it is reasserted that the claims are obvious over the Hernandez reference.

As stated in previous Office Actions, Hernandez teaches a starch fiber diameter of 10-500 microns rather than the presently claimed less than 10 microns. However, it is argued that the claims are obvious over the teachings of Hernandez. Specifically, it has been held that discovering an optimum value of a result effective variable involves only routine skill in the art. *In re Boesch*, 205 USPQ 215. In the instant case, decreasing the fiber diameter will produce a softer, more absorbent product. Therefore, said claims are rejected as being obvious over the cited Hernandez reference.

Art Unit: 1771

8. Applicant also argues that Hernandez “only teaches making one diameter of starch fiber; namely, a fiber having an average fiber diameter of 65 μm ” (paragraph spanning 1st and 2nd pages of Remarks). This statement is incorrect since Hernandez explicitly teaches the starch fiber may be 10-500 microns in diameter (col. 3, lines 59-61). Applicant also asserts “Hernandez never explicitly teaches or enables one of ordinary skill in the art how to make a starch fiber having a diameter of less than 10 μm using its solvent spinning process” (paragraph spanning 1st and 2nd pages of Remarks). In response, Hernandez is not required to have such a teaching since the rejection is not a 102 anticipation rejection.

9. Additionally, applicant argues its method of solvent spinning to produce the fiber of the claimed diameter and the flexibility properties obtained from such a fiber diameter (Remarks, page 2). It is noted that the features upon which applicant relies (i.e., method of making and properties thereof) are not recited in the rejected claims. Although the claims are interpreted in light of the specification, limitations from the specification are not read into the claims. See *In re Van Geuns*, 988 F.2d 1181, 26 USPQ2d 1057 (Fed. Cir. 1993). Therefore, applicant’s arguments are found unpersuasive and the above rejection stands.

10. Regarding the Mackey Declaration under 1.132, said declaration is insufficient to overcome the prior art rejections. Specifically, said declaration is insufficient for the reasons set forth above for why applicant’s arguments are not found persuasive. Additionally, said declaration is not commensurate in scope with the present claims. In other words, applicant is not claiming a method of making the starch fiber, including the “extremely high attenuation forces,” but rather applicant is merely claiming a fiber having a specified diameter. Therefore, said declaration is insufficient and the above rejection stands.

Conclusion

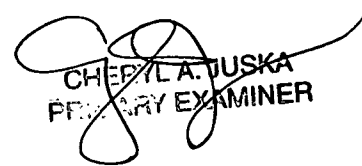
11. This is an RCE of applicant's earlier Application No. 09/914,966. All claims are drawn to the same invention claimed in the earlier application (i.e., Amendment filed September 27, 2004) and were finally rejected on the grounds and art of record in the Office Action of December 10, 2004. Accordingly, **THIS ACTION IS MADE FINAL** even though it is a first action in this case. See MPEP § 706.07(b). Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

12. A shortened statutory period for reply to this final action is set to expire **THREE MONTHS** from the mailing date of this action. In the event a first reply is filed within **TWO MONTHS** of the mailing date of this final action and the advisory action is not mailed until after the end of the **THREE-MONTH** shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no, however, event will the statutory period for reply expire later than **SIX MONTHS** from the mailing date of this final action.

13. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Cheryl Juska whose telephone number is 571-272-1477. The examiner can normally be reached on Monday-Friday 10am-6pm. If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Terrel Morris can be reached at 571-272-1478. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Art Unit: 1771

14. Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).


CHERYL A. JUSKA
PRIMARY EXAMINER



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
09/914,966	09/06/2001	Larry Neil Mackey	U 013595-2	6640

27752 7590 09/16/2005

THE PROCTER & GAMBLE COMPANY
INTELLECTUAL PROPERTY DIVISION
WINTON HILL TECHNICAL CENTER - BOX 161
6110 CENTER HILL AVENUE
CINCINNATI, OH 45224

EXAMINER

JUSKA, CHERYL ANN

ART UNIT	PAPER NUMBER
----------	--------------

1771

DATE MAILED: 09/16/2005

Please find below and/or attached an Office communication concerning this application or proceeding.

Office Action Summary

Application No.

09/914,966

Applicant(s)

MACKEY ET AL.

Examiner

Cheryl Juska

Art Unit

1771

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

- 1) ☒ Responsive to communication(s) filed on 29 June 2005.
- 2a) ☒ This action is **FINAL**. 2b) ☐ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

- 4) ☒ Claim(s) 11-18 and 20-32 is/are pending in the application.
- 4a) Of the above claim(s) _____ is/are withdrawn from consideration.
- 5) ☐ Claim(s) _____ is/are allowed.
- 6) ☒ Claim(s) 11-18 and 20-32 is/are rejected.
- 7) ☐ Claim(s) _____ is/are objected to.
- 8) ☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on _____ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

- 12) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All b) ☐ Some * c) ☐ None of:
- ☐ Certified copies of the priority documents have been received.
 - ☐ Certified copies of the priority documents have been received in Application No. _____.
 - ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

- | | |
|--|---|
| 1) <input type="checkbox"/> Notice of References Cited (PTO-892) | 4) <input type="checkbox"/> Interview Summary (PTO-413)
Paper No(s)/Mail Date. _____ |
| 2) <input type="checkbox"/> Notice of Draftsperson's Patent Drawing Review (PTO-948) | 5) <input type="checkbox"/> Notice of Informal Patent Application (PTO-152) |
| 3) <input type="checkbox"/> Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08)
Paper No(s)/Mail Date _____ | 6) <input type="checkbox"/> Other: _____ |

DETAILED ACTION

Response to Amendment

1. Applicant's amendment filed June 29, 2005, has been entered. Claims 1-10 and 19 are cancelled. Claims 11, 29, and 30 are amended as requested. Thus, the pending claims are 11-18 and 20-32.

Claim Rejections - 35 USC § 103

2. The text of those sections of Title 35, U.S. Code not included in this action can be found in a prior Office action.

3. Claims 11-12, 15-18, 20-32 stand rejected under 35 USC 103(a) as being unpatentable over US 4,243,480 issued to Hernandez et al. as set forth in sections 4, 6, and 7 of the last Office Action.

Applicant has amended the claims to limit the average fiber diameter to less than 5 microns. While Hernandez teaches a fiber diameter of 10-500 microns, it is argued that employing a fiber diameter of less than 5 microns or less would still be obvious to one skilled in the art. Specifically, it has been held that discovering an optimum value of a result effective variable involves only routine skill in the art. *In re Boesch*, 205 USPQ 215. Smaller fiber diameters would increase the total fiber surface area of the fibrous structure, thereby enhancing absorbency and hand. Additionally, applicant has not provided evidence of any criticality for or unexpected results obtained by the claimed fiber diameter. Thus, it is believed the claimed range is obvious over the prior art.

Art Unit: 1771

4. Claim 14 stands rejected under 35 USC 103(a) as being unpatentable over the cited Hernandez reference in view of US 5,516,815 issued to Buehler et al. for the reasons of record.

Response to Arguments

5. Applicant traverses the above rejections by asserting that the claimed invention is “not rendered obvious over Hernandez because Hernandez fails to teach each and every element of claims 11, 29, and 30, as amended (Amendment, page 5, 4th paragraph). In response, the examiner agrees that Hernandez does not teach “each and every element” of the claimed invention. As such, the rejection is not a 102 anticipation rejection, but rather a 103 rejection. However, it is reasserted that the claims are obvious over the Hernandez reference. As discussed above, it would have been obvious to one of ordinary skill in the art to select a fiber diameter less than 5 microns since it has been held that discovering an optimum value of a result effective variable involves only routine skill in the art. Additionally, it is noted that the capability of producing finer fibers has greatly improved in recent years. Said fibers have improved properties, such as soft hand, good absorbency, etc. Therefore, applicant’s arguments are found unpersuasive and the above rejection stands.

Conclusion

6. **THIS ACTION IS MADE FINAL.** Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire **THREE MONTHS** from the mailing date of this action. In the event a first reply is filed within **TWO**

Art Unit: 1771

MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the mailing date of this final action.

7. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Cheryl Juska whose telephone number is 571-272-1477. The examiner can normally be reached on Monday-Friday 10am-6pm. If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Terrel Morris can be reached at 571-272-1478. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

8. Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

cj
September 14, 2005

CHERYL A. JUSKA
PRIMARY EXAMINER

- 60 -

ABSTRACT

A flexible absorbent structure is produced comprising starch fibers. Naturally occurring starch in the presence of water, plasticizers and other additives is melt extruded and spun bonded to form low density, absorbent, flexible structures. The structures exhibit properties matching those of consumer paper products such as paper towels, toilet tissue, facial tissue, napkins, wet wipes, and the like.

PCT/IB00/00234

- 1 -

ABSORBENT, FLEXIBLE, STRUCTURE COMPRISING STARCH FIBERSFIELD OF THE INVENTION

The present invention relates to pseudo-thermoplastic starch extruded in the form of fibers. Starch may be extruded and either meltblown or spunbonded to form fibrous low density structures.

BACKGROUND OF THE INVENTION

It is well recognized that starch molecules come in two forms: the substantially linear amylose polymer and the highly branched amylopectin polymer. These two forms of starch have very different properties, probably due to the ease of association of the hydroxyl groups among different molecules. The molecular structure of amylose is essentially linear with two to five relatively long branches. The average degree of polymerization of the branches is about 350 monomer units. Under conditions that provide sufficient freedom of molecular movements, primarily by dilution with suitable solvents, and in some instances, dilution coupled with heating, the linear amylose chains can be oriented into preferentially parallel alignments such that the hydroxyl groups on one chain are in close proximity with those on the adjacent chains. The alignment of neighboring amylose molecules is believed to facilitate intermolecular hydrogen bonding. Consequently the amylose molecules form strong aggregates. In contrast, the molecular structure of amylopectin is highly branched via 1,6- α linkages. The average degree of polymerization of the branches is about 25 monomer units. Due to the highly branched structure, the amylopectin molecules can not move as freely and do not align and associate as readily.

Attempts have been made to process natural starch on standard equipment and existing technology known in the plastic industry. Since natural starch generally has a granular structure, it needs to be "destructurized" and/or modified before it can be melt processed like a thermoplastic material. For destructurization, the starch is typically heated above its softening and melting temperature under a pressurized condition. Melting and disordering of the molecular structure of the starch granule takes place and a destructurized starch is obtained. Chemical or enzymatic agents may also be used to destructurize, oxidize, or derivatize the starch. Modified starches have been used to make biodegradable plastics, wherein the modified starch is

- 2 -

blended as an additive or the minor component with petroleum-based or synthetic polymers. However, when the modified starch is processed by itself or as the major component in a blend with other materials using conventional thermoplastic processing techniques, such as molding or extrusion, the finished parts tend to have a high incidence of defects. Moreover, the modified starch (alone or as the major component of a blend) has been found to have poor melt extensibility; consequently, it cannot be successfully processed by uniaxial or biaxial extensional processes into fibers, films, foams or the like.

Previous attempts to produce starch fibers relate principally to wet-spinning processes. For Example, a starch/solvent colloidal suspension can be extruded from a spinneret into a coagulating bath. This process relies on the marked tendency of amylose to align and form strongly associated aggregates to provide strength and integrity to the final fiber. Any amylopectin present is tolerated as an impurity that adversely affects the fiber spinning process and the strength of the final product. Since it is well known that natural starch is rich in amylopectin, earlier approaches include pre-treating the natural starch to obtain the amylose-rich portion desirable for fiber spinning. Clearly this approach is not economically feasible on a commercial scale since a large portion (i.e, the amylopectin portion) of the starch is discarded. In more recent developments, natural starch, typically high in natural amylopectin content, can be wet-spun into fibers. However, the wet-spun fibers are coarse, typically having fiber diameters greater than 50 microns. Additionally, the large quantity of solvent used in this process requires an additional drying step and a recovery or treatment step of the effluent. Some references for wet-spinning starch fibers include U.S. Patent No. 4,139,699 issued to Hernandez et al. on February 13, 1979; U.S. Patent No. 4,853,168 issued to Eden et al. on August 1, 1989; and U.S. Patent No. 4,234,480 issued to Hernandez et al. on January 6, 1981.

U.S. Patent Nos. 5,516,815 and 5,316,578 to Buehler et al. relate to starch compositions for making starch fibers from a melt spinning process. The melt starch composition is extruded through a spinnerette to produce filaments having diameters slightly enlarged relative to the diameter of the die orifices on the spinnerette (i.e., a die swell effect). The filaments are subsequently drawn down mechanically or

- 3 -

thermomechanically by a drawing unit to reduce the fiber diameter. The major disadvantage of the starch composition of Buehler et al. is that it does not use high molecular weight polymers, which enhance the melt extensibility of starch compositions. Consequently, the starch composition of Buehler et al. could not be
5 successfully melt attenuated to produce fine fibers of 25 microns or less in diameter.

Other thermoplastically processable starch compositions are disclosed in U.S. Patent No. 4,900,361, issued on August 8, 1989 to Sachetto et al.; U.S. Patent No. 5,095,054, issued on March 10, 1992 to Lay et al.; U.S. Patent No. 5,736,586, issued on April 7, 1998 to Bastioli et al.; and PCT publication WO 98/40434 filed by
10 Hanna et al. published March 14, 1997. These starch compositions do not contain the high molecular weight polymers that are necessary to achieve the desired melt viscosity and melt extensibility, which are critical material characteristics to producing fine fibers, thin films or thin-walled foams.

Cellulose fibrous webs such as paper are well known in the art. Low
15 density fibrous webs are in common use today in products such as paper towels, toilet tissue, facial tissue, napkins, wet wipes, and the like. The large demand for such paper products has created a need for improvements in the products and in the methods of their manufacture.

There are several well known concerns regarding the papermaking
20 industry requiring papermaking manufacturers to balance the costs of machinery and resources with the total cost of delivering the paper products to the consumers. First instance, the popularity of paper products has created an increasing demand on wood based cellulosic fibers resulting in a rapid depletion of trees due to deforestation.

In addition, during conventional papermaking operations wood
25 cellulosic fibers are repulped, beaten or refined to achieve a level of fiber hydration in order to form an aqueous pulp slurry. Processes for the making of paper products for use in tissue, toweling, and sanitary products generally involve the preparation of the aqueous slurry and then subsequently removing the water from the slurry while contemporaneously rearranging the fibers therein to form a paper web. Subsequent to
30 dewatering, the web is processed into a dry roll or sheet form and eventually converted into a consumer package. Various types of machinery must be employed to assist in

- 4 -

the dewatering process and converting operations requiring a significant investment in capital.

Further, the conventional papermaking operation involves the incorporation of additives into the pulp in order to achieve specific end properties. For instance, additives such as strength resins, debonding surfactants, softening agents, pigments, lattices, synthetic microspheres, fire-retardants, dyes, perfumes, etc., are often employed in the manufacture of paper. The efficient retention of these additives at the wet end of a papermaking process presents difficulty to the manufacturer since that portion which is not retained creates not only an economic loss but also significant pollution problems if it becomes part of a plant effluent. Additives can also be added to the paper web subsequent to dewatering via coating or saturation processes commonly known in the art. These processes usually require that excess heating energy be consumed to redry the paper after coating. Moreover, in some instances, the coating systems are required to be solvent based which increases capital costs and requires recovery of volatile materials to meet regulatory requirements.

Various natural fibers other than cellulose as well as a variety of synthetic fibers have been employed in making paper. However, these replacements have failed to provide a commercially acceptable substitute for cellulose due to their high cost, poor bonding properties, chemical incompatibilities, and handling difficulties in papermaking systems. Starch fibers have been suggested as a substitute for cellulose in various aspects of the papermaking process, however, commercial attempts to use such fibers have been unsuccessful. As a result, paper products are still being manufactured almost exclusively from wood base cellulosic ingredients.

Starch is a plant carbohydrate having a structure analogous to cellulose. Whereas cellulose is a polymer of D-glucan monomers connected via 1,4- β linkages, starch is a polymer of D-glucose monomers connected via primarily 1,4- α linkages. Because starch is available via agricultural resources, it is cheap and plentiful. While starch has been incorporated into various aspects of the papermaking process, attempts to use starch fibers as cellulose fiber replacement in commercial papermaking processes have not been successful.

Consequently, there is a need for an inexpensive and melt processable

- 5 -

composition from natural starches. Such a melt processable starch composition should not require evaporation of a large quantity of solvents or produce a large amount of effluent during the processing operation. Moreover, such a starch composition should have melt rheological properties suitable for use in conventional plastic processing equipment

There is also a need for a starch composition suitable for use in uniaxial or biaxial extensional processes to produce fibers, films, sheets, foams, shaped articles, and the like economically and efficiently. Specifically, the starch composition should have melt rheological properties suitable for uniaxially or biaxially extensional processes in its melt phase in a substantially continuous manner, i.e., without excessive amount of melt fracture or other defects.

Further, there is a need for a low density flexible structure comprising starch fibers utilizing extrusion and fiber spinning techniques. Particularly, a low density flexible structure comprising starch fibers, wherein the structure has improved tensile strength, softness, and absorbency properties relative to cellulosic pulp fiber structures and the like, while maintaining biodegradability and flushability.

SUMMARY OF THE INVENTION

The present invention provides an absorbent flexible structure comprising starch fibers. Naturally occurring starch in the presence of water, plasticizers and other additives is melt extruded and spun into fibers to form an absorbent flexible structure having an apparent density ranging from 0.02 g/cm³ to 0.20 g/cm³ and a basis weight ranging from 10 g/m² to 450 g/m².

The starch fibers making up the structure can have a size ranging from about 0.01 decitex to about 135 decitex. In a preferred embodiment the fibers can have a size ranging from about 0.02 decitex to about 30 decitex, and most preferably ranging from about 0.02 to about 5 decitex. In addition, fibers making up the structure of the present invention can have a glass transition temperature ranging from about -30 °C to about 150 °C, more preferably from about -30 °C to about 100 °C, and most preferably from about -30 °C to about 25 °C.

Exemplary physical properties of the flexible structure of the present invention include dry tensile strength and wet tensile strength. The dry tensile strength

- 6 -

of the structure, which is measured as a geometric mean tensile strength, can range from about 10 g/cm to about 1200 g/cm, more preferably from about 30 g/cm to about 600 g/cm, and most preferably from about 40 g/cm to about 475 g/cm. The wet tensile strength of the structure, which is also measured as a geometric mean tensile strength, can range from about 2 g/cm to about 400 g/cm, and more preferably from about 2 g/cm to about 200 g/cm.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other features, aspects and advantages of the present invention will become better understood with regard to the following description, appended claims, and accompanying drawings where:

Figure 1a illustrates a torque rheometer assembly used to produce starch fibers.

Figure 1b illustrates the twin screw elements attached to the drive unit and disposed within the barrel of the torque rheometer assembly illustrated in Figure 1a.

Figure 1c shows a torque rheometer assembly having a melt blowing die used to produce fine starch fibers of the present invention.

Figure 2a illustrates a vented twin screw extruder assembly.

Figure 2b illustrates the screw and mixing element configuration for the extrusion assembly depicted in Figure 2a.

Figure 3a illustrates a non-vented twin screw extruder assembly.

Figure 3b illustrates the screw and mixing element configuration for the extrusion assembly depicted in Figure 3a.

Figure 4 illustrates a spinneret and a drawing unit used for pseudo-thermoplastic starch melt fiber spinning.

Figure 5 illustrates the sample rack and cover used for determining absorbency of the starch fiber structures.

Figure 6 illustrates the cross section of the frames for the sample rack and cover illustrated in Figure 5.

Figure 7a is the Scanning Electron Micrographs of fine starch fibers of the present invention shown on a 200 micron scale.

- 7 -

Figure 7b is the Scanning Electron Micrographs of fine starch fibers of the present invention shown on a 20 micron scale.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

5 As used herein, the following terms have the following meanings:

Pseudo-thermoplastic composition is intended to denote materials which by the influence of elevated temperatures may be softened to such a degree that they can be brought into a flowable state, and in this condition may be shaped as desired. Pseudo-thermoplastic materials may be formed under simultaneous influence
10 of heat and pressure. Pseudo-thermoplastic compositions differ from thermoplastic compositions in that the softening or liquefying of the pseudo-thermoplastic is caused by softeners or solvents present without which it would be impossible to bring them by any temperature or pressure into a soft or flowable condition necessary for shaping since pseudo thermoplastics do not melt as such. The influence of water content on
15 the glass transition temperature and melting temperature of starch can be measured by differential scanning calorimetry as described by Zeleznak and Hoseny "Cereal Chemistry", Vol. 64, No. 2, pp. 121-124, 1987.

Pseudo-thermoplastic melt is a pseudo-thermoplastic material in a flowable state.

20 Glass transition temperature, T_g , is the temperature at which the material changes from a viscous or rubbery condition to a hard and relatively brittle condition.

Basis weight is the weight (in grams) per unit area (in square meters) of a sample reported in grams per square meter.

25 Caliper is the macroscopic thickness of a sample measured as described below.

Apparent density is the basis weight of the sample divided by the caliper with appropriate unit conversions incorporated therein. Apparent density used herein has the units of grams / centimeters cubed (g/cm^3).

30 Machine direction, designated MD, is the direction parallel to the flow of the starch fiber structure through the product manufacturing equipment.

- 8 -

Cross machine direction, designated CD, is the direction perpendicular to the machine direction in the same plane of the starch fiber structure.

Geometric Mean Dry Tensile Strength (GMDT) is the square root of the product of the machine and cross-machine dry tensile strengths (in grams/cm). The value of GMDT is reported in grams/cm.

Geometric mean wet tensile strength (GMWT) is the square root of the product of the machine and cross-machine wet tensile strengths (in grams/cm). The value of GMWT is reported in grams/cm.

Structure is an arrangement of one or more parts forming a substance or body.

Absorbency is the ability of a material to take up fluids by various means including capillary, osmotic, solvent or chemical action and retain such fluids.

Flexibility indicates the capability of being deformed under a given load without being broken and with or without returning of itself to its former shape.

A fiber is a slender object having a major axis which is very long compared to the two orthogonal axes and having an aspect ratio of at least 4/1, preferably at least 10/1.

Decitex, dtex, is a unit of measure for a fiber expressed in

grams
10,000 meters

Flushability is determined by the geometric mean decayed wet tensile strength (GMDWT) (defined below). A flushable structure has a geometric mean decayed wet tensile of less than about 20 g/cm and more preferably less than about 10 g/cm.

The term "bound water" means the water found naturally occurring in starch and before mixing of starch with other components to make the composition of the present invention. The term "free water" means the water that is added in making the composition of the present invention. A person of ordinary skill in the art would recognize that once the components are mixed in a composition, water can no longer be distinguished by its origin.

All percentages, ratios and proportions used herein are by weight

- 9 -

percent of the composition, unless otherwise specified.

The specification contains a detailed description of (1) exemplary materials of the present invention, (2) exemplary processes for producing the present invention, (3) material properties of the present invention, and (4) analytical procedures for measuring properties of the present invention

(1) Exemplary Materials

For the present invention a starch polymer is mixed with water, plasticizers and other additives and melt extruded to produce fibers . Standard meltblowing or spunbonding techniques are used to produce starch fiber structures.

Such structures may be absorbent and flexible. These structures may be used as substitutes for paper products such as paper towels, napkins, toilet tissues, facial tissues, place mats and wet wipes. Other uses include, but are not limited to, oil absorbents, seed carriers, fillers for concrete, pressed board, and other construction materials, time released watering aids for house plants, and thin films.

The starch fibers of the present invention may be useful for forming fibrous structures and also forming absorbent materials, as described above. The absorbent structures/fibrous materials comprising the starch fibers of the present invention may have from a trace amount to one hundred percent (100%) starch fibers, or a blend of starch fibers and other suitable fibers. Other suitable fibers for the blend include cellulose fibers, synthetic fibers, and a combination thereof.

Starch polymers can include any naturally occurring (unmodified) starch, physically modified starch, chemically modified starch, biologically modified starch or combinations thereof.

Naturally occurring starch is generally a mixture of linear amylose and branched amylopectin polymer of D-glucose units. The amylose is a substantially linear polymer of D-glucose units joined by (1,4)- α -D links. The amylopectin is a highly branched polymer of D-glucose units joined by (1,4)- α -D links and (1,6)- α -D links at the branch points. Naturally occurring starch typically contains relatively high amylopectin, for example, corn starch (64-80% amylopectin), waxy maize (93-100% amylopectin), rice (83-84% amylopectin), potato (about 78% amylopectin), and wheat (73-83% amylopectin). Though all starches are useful herein, the present invention is

- 10 -

most commonly practiced with high amylopectin natural starches derived from agricultural sources, which offer the advantages of being abundant in supply, easily replenishable and inexpensive in price.

Suitable naturally occurring starches can include, but are not limited to, corn starch, potato starch, sweet potato starch, wheat starch, sago palm starch, tapioca starch, rice starch, soybean starch, arrow root starch, bracken starch, lotus starch, waxy maize starch, high amylose corn starch, and commercial amylose powder. Naturally occurring starches particularly, corn starch and wheat starch, are the preferred starch polymers of choice due to their economy and availability.

Physically modified starch is formed by changing the dimensional structure. Physical modifications of the starch may be intramolecular or intermolecular modifications. Intramolecular modifications include reduced molecular weight and/or molecular weight distribution, changes in the polymer chain conformation, and the like. Intermolecular modifications include melting and/or disordering the starch molecules, reduction in crystallinity, crystallite size, and granular size, and the like. These physical modifications may be achieved by input of energy (such as thermal, mechanical, thermomechanical, electromagnetic, ultrasonic, and the like), pressure, moisture, fractionation, and combinations thereof. Physically modified starch can include α starch, fractionated starch, moisture and heat treated starch.

Chemical modifications of starch typically include acid or alkali hydrolysis and oxidative chain scission to reduce molecular weight and molecular weight distribution. Suitable compounds for chemical modification of starch include organic acid such as citric acid, acetic acid, glycolic acid, and adipic acid; inorganic acids such as hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid boric acid, and partial salts of polybasic acids, e.g., KH_2PO_4 , NaHSO_4 ; group Ia or IIa metal hydroxides such as sodium hydroxide, potassium hydroxide; ammonia; oxidizing agents such as hydrogen peroxide, benzoyl peroxide, ammonium persulfate, potassium permagnate, sodium bicarbonate, hypochloric salts, and the like; and mixtures thereof. Preferred chemical agents or the present invention include ammonium persulfate, sulfuric acid, hydrochloric acid, and mixtures thereof.

Chemically modified starch may be formed by reaction of its OH

- 11 -

groups with alkylene oxides, and other ether-, ester-, urethane-, carbamate-, or isocyanate- forming substances. Hydroxyalkyl, acetyl, or carbamate starches or mixtures thereof are preferred chemically modified starches. The degree of substitution of the chemically modified starch is 0.05 to 3.0, preferably 0.05 to 0.2.

5 Biological modifications of starch include bacterial digestion of the carbohydrate bonds, or enzymatic hydrolysis using enzymes such as amylase, amylopectase, and the like.

 The starch desirably has a bound water content of about 5% to 16% by weight of starch. A water content of 8% to 12% by weight of starch is particularly
10 preferred. The amylose content of the starch is 0% to 80% by weight of starch, preferably 20% to 30% by weight of starch.

 Natural, unmodified starch generally has a very high average molecular weight and a broad molecular weight distribution (e.g. natural corn starch has an average molecular weight of about 60,000,000 and a molecular weight distribution
15 greater than 1000). The average molecular weight of starch can be reduced to the desirable range for the present invention by chain scission (oxidative or enzymatic), hydrolysis (acid or alkaline catalyzed), physical/mechanical degradation (e.g., via the thermomechanical energy input of the processing equipment), or combinations thereof. These reactions also reduce the molecular weight distribution of starch to less than
20 about 600, preferably to less than about 300. The thermomechanical method and the oxidation method offer an additional advantage, carried out in situ of the melting spinning process.

 In one embodiment, the natural starch is hydrolyzed in the presence of acids, such as hydrochloric acid or sulfuric acid, to reduce the molecular weight and
25 molecular weight distribution. In another embodiment, a chain scission agent may be incorporated into the melt spinnable starch composition such that the chain scission reaction takes place substantially concurrently with the blending of the starch with other components. Nonlimiting examples of oxidative chain scission agents suitable for use herein include ammonium persulfate, hydrogen peroxide, hypochloric salts,
30 potassium permanganate, and mixtures thereof. Typically, the chain scission agent is added in an amount effective to reduce the weight-average molecular weight of the

- 12 -

starch to the desirable range. For example, it is found that for uniaxial or biaxial melt attenuation processes, the starch should have a weight-average molecular weight ranging from about 1,000 to about 2,000,000, preferably from about 1,500 to about 800,000, more preferably from about 2,000 to about 500,000. It is found that compositions having modified starch in the above molecular weight range have a suitable melt shear viscosity, and thus, improved melt processability. The improved melt processability is evident in less interruptions of the process (e.g., reduced breakage, shots, defects, hang-ups) and better surface appearance and strength properties of the product.

Typically, the composition herein comprises from about 20 to about 99.99 wt%, preferably from about 30 to about 95 wt%, and more preferably from about 50 to about 85 wt%, of unmodified and/or modified starch. The weight of starch in the composition includes starch and its naturally occurring bound water content. It is known that additional free water may be incorporated as the polar solvent or plasticizer, and not included in the weight of the starch.

High molecular weight polymers (hereinafter "high polymers") which are substantially compatible with starch are also useful herein. The molecular weight of a suitable polymer should be sufficiently high to effectuate entanglements and/or associations with starch molecules. The high polymer preferably has a substantially linear chain structure. Though a linear chain having short (C1-C3) branches or a branched chain having one to three long branches are also suitable for use herein. As used herein, the term "substantially compatible" means when heated to a temperature above the softening and/or the melting temperature of the composition, the high polymer is capable of forming a substantially homogeneous mixture with the starch (i.e., the composition appears transparent or translucent to the naked eyes).

The Hildebrand solubility parameter (δ) can be used to estimate the compatibility between starch and the polymer. Generally, substantial compatibility between two materials can be expected when their solubility parameters are similar. It is known that water has a δ_{water} value of $48.0 \text{ MPa}^{1/2}$, which is the highest among common solvents, probably due to the strong hydrogen bonding capacity of water. Starch typically has a δ_{starch} value similar to that of cellulose (about $344 \text{ MPa}^{1/2}$).

- 13 -

Without being bound by theory, it is believed that polymer suitable for use herein preferably interact with the starch molecules on the molecular level in order to form a substantially compatible mixture. The interactions range from the strong, chemical type interactions such as hydrogen bonding between polymer and starch, to merely physical entanglements between them. The polymers useful herein are preferably high molecular weight, substantially linear chain molecules. The highly branched structure of an amylopectin molecule favors the branches to interact intramolecularly, due to the proximity of the branches within a single molecule. Thus, it is believed that the amylopectin molecule has poor or ineffective entanglements/interactions with other starch molecules, particularly other amylopectin molecules. The compatibility with starch enables suitable polymers to be intimately mixed and chemically interact and/or physically entangle with the branched amylopectin molecules such that the amylopectin molecules associate with one another via the polymers. The high molecular weight of the polymer enables it to simultaneously interact/entangle with several starch molecules. That is, the high polymers function as molecular links for starch molecules. The linking function of the high polymers is particularly important for starches high in amylopectin content. The entanglements and/or associations between starch and polymers enhance the melt extensibility of the starch composition such that the composition is suitable for extensional processes. In one embodiment, it is found that the composition can be melt attenuated uniaxially to a very high draw ratio (greater than 1000).

In order to effectively form entanglements and/or associations with the starch molecules, the high polymer suitable for use herein should have a weight-average molecular weight of at least 500,000. Typically the weight average molecular weight of the polymer ranges from about 500,000 to about 25,000,000, preferably from about 800,000 to about 22,000,000, more preferably from about 1,000,000 to about 20,000,000, and most preferably from about 2,000,000 to about 15,000,000. The high molecular weight polymers are preferred due to the ability to simultaneously interact with several starch molecules, thereby increases extensional melt viscosity and reduces melt fracture.

Suitable high polymers have a δ polymer such that the difference

- 14 -

between δ starch and δ polymer is less than about $10 \text{ MPa}^{1/2}$, preferably less than about $5 \text{ MPa}^{1/2}$, and more preferably less than about $3 \text{ MPa}^{1/2}$. Nonlimiting examples of suitable high polymers include polyacrylamide and derivatives such as carboxyl modified polyacrylamide, acrylics and acrylic polymers and copolymers including polyacrylic acid, polymethacrylic acid, and their partial esters; vinyl polymers including polyvinyl alcohol, polyvinylacetate, polyvinylpyrrolidone, polyethylene vinyl acetate, polyethyleneimine, and the like; polyamides; polyalkylene oxides such as polyethylene oxide, polypropylene oxide, polyethylenepropylene oxide, and mixtures thereof. Copolymers made from mixtures of monomers selected from any of the aforementioned polymers are also suitable herein. Other exemplary high polymers include water soluble polysaccharides such as alginates, carrageenans, pectin and derivatives, chitin and derivatives, and the like; gums such as guar gum, xanthum gum, agar, gum arabic, karaya gum, tragacanth gum, locust bean gum, and like gums; water soluble derivatives of cellulose, such as alkylcellulose, hydroxyalkylcellulose, carboxymethylcellulose, and the like; and mixtures thereof.

Some polymers (e.g., polyacrylic acid, polymethacrylic acid) are generally not available in the high molecular weight range (i.e., 500,000 or higher). A small amount of crosslinking agents may be added to create branched polymers of suitably high molecular weight useful herein.

The high polymer is added to the composition of the present invention in an amount effective to visibly reduce the melt fracture and capillary breakage of fibers during the spinning process such that substantially continuous fibers having relatively consistent diameter can be melt spun. These polymers are typically present in the range from about 0.01 to about 10 wt%, preferably from about 0.03 to about 1 wt%, more preferably from about 0.05 to about 0.5 wt% of the composition. It is surprising to find that at a relatively low concentration, these polymers significantly improves the melt extensibility of the starch composition.

The starch compositions may optionally include additives to enhance melt flow and melt processability, particularly the extensibility of the composition under the melt processing conditions. The additives may function as plasticizers and/or diluents to reduce the melt shear viscosity of the starch composition. The

- 15 -

plasticizers are added to the composition of the present invention in an amount effective to improve the flow, hence, the melt processability. The plasticizers may also improve the flexibility of the final products, which is believed to be due to the lowering of the glass transition temperature of the composition by the plasticizer. The plasticizers should preferably be substantially compatible with the polymeric components of the present invention so that the plasticizers may effectively modify the properties of the composition. As used herein, the term "substantially compatible" means when heated to a temperature above the softening and/or the melting temperature of the composition, the plasticizer is capable of forming a substantially homogeneous mixture with starch (i.e., the composition appears transparent or translucent to the naked eye).

A plasticizer is typically added to the starch polymer in order to lower the glass transition temperature of the starch fibers thereby enhancing the flexibility of the fibers. In addition, the presence of the plasticizer lowers the melt viscosity which in turn facilitates the melt extrusion process. The plasticizer is advantageously an organic compound having at least one hydroxyl group, preferably a polyol. Without being bound by theory, it is believed that the hydroxyl groups of the plasticizers enhance compatibility by forming hydrogen bonds with the starch matrix material. Nonlimiting examples of useful hydroxyl plasticizers include sugars such as glucose, sucrose, fructose, raffinose, maltodextrin, galactose, xylose, maltose, lactose, mannose erythrose, glycerol, and pentaerythritol; sugar alcohols such as erythritol, xylitol, malitol, mannitol and sorbitol; polyols such as ethylene glycol, propylene glycol, dipropylene glycol, butylene glycol, hexane triol, and the like, and polymers thereof; and mixtures thereof.

Also useful herein as hydroxyl plasticizers are poloxomers (polyoxyethylene/polyoxypropylene block copolymers) and poloxamines (polyoxyethylene/polyoxypropylene block copolymers of ethylene diamine). Suitable "poloxomers" comprise block copolymers of polyoxyethylene/polyoxypropylene having the following structure:

$$\text{HO} - (\text{CH}_2 - \text{CH}_2 - \text{O})_x - (\text{CHCH}_3 - \text{CH}_2 - \text{O})_y - (\text{CH}_2 - \text{CH}_2 - \text{O})_z - \text{OH}$$
wherein x has a value ranging from about 2 to about 40, y has a value ranging from

- 16 -

about 10 to about 50, and z has a value ranging from about 2 to about 40, and preferably x and z have the same value. These copolymers are available as Pluronic® from BASF Corp., Parsippany, NJ. Suitable poloxamers and poloxamines are available as Synperonic® from ICI Chemicals, Wilmington, DE, or as Tetronic® from
5 BASF Corp., Parsippany, NJ.

Also suitable for use herein as hydroxyl-free plasticizers are other hydrogen bond forming organic compounds which do not have hydroxyl group, including urea and urea derivatives; anhydrides of sugar alcohols such as sorbitan; animal proteins such as gelatin; vegetable proteins such as sunflower protein, soybean
10 proteins, cotton seed proteins; and mixtures thereof. All of the plasticizers may be use alone or in mixtures thereof.

Typically, the hydroxyl plasticizer comprises from about 5 wt% to about 70 wt%, more preferably from about 15 wt% to about 60 wt%, most preferably from about 30 wt% to about 40 wt% of the starch composition. The hydroxyl-free
15 plasticizer typically comprises from about 0.1 wt% to about 70 wt%, preferably from about 5 wt% to about 65 wt%, more preferably from about 20 wt% to about 60 wt% of the starch composition.

In one embodiment, a mixture of the hydroxyl and hydroxyl-free plasticizers is used, wherein the hydroxyl plasticizers are sugars, such as sucrose, fructose, and sorbitol, and the hydroxyl-free plasticizers are urea and urea derivatives.
20 It is found that urea and its derivatives in the starch composition of the present invention have a strong tendency to crystallize, that is, crystallization of urea and its derivatives occurs even under fast cooling condition such as melt blowing, spun bonding, melt extrusion, wet spinning, and the like. Therefore, urea and urea
25 derivatives may be used as solidifying agents for modifying or controlling the solidification rate of the starch composition of the present invention. In a preferred embodiment, a mixture of sucrose and urea is added to the starch/polymer composition in an amount effective to achieve the desired melt processability and cooling rate.

Diluents may be added to the starch compositions of the present
30 invention to adjust the melt shear viscosity and enhance the melt spinnability of the starch compositions. Generally, the melt shear viscosity decreases in a nonlinear

- 17 -

manner as the polar solvent content is increased. Typically, the polar solvent is added in an amount from about 5 wt% to about 40 wt%, preferably from about 7 wt% to about 30 wt%, more preferably from about 10 wt% to about 20 wt%, of the total composition.

5 Suitable for use herein as diluents are polar solvents having a solubility parameter δ ranging from about 19 to about 48 MPa^{1/2}, preferably from about 24 to about 48 MPa^{1/2}, and more preferably from about 28 to about 48 MPa^{1/2}. Nonlimiting examples include water, C1-C18 linear or branched alcohols, DMSO (dimethyl sulphoxide), formamide and derivatives such as N-methyl formamide, N-ethyl
10 formamide, acetamide and derivatives such as methyl acetamide, Cellosolv® (a glycol alkyl ether) and derivatives, such as butyl Cellosolv®, benzyl Cellosolv®, Cellosolv® acetate (all Cellosolv® and derivatives are available from J. T. Baker, Phillipsburg, NJ), hydrazine, and ammonia. It is also known that the δ value of a solvent mixture can be determined by volume-averaging the δ values of the individual solvents.

15 Therefore, mixed solvents having δ values within the above-identified range (i.e., from about 19 to about 48 MPa^{1/2}) are also suitable for use herein. For example, a mixed solvent of DMSO/water having a composition of 90/10 v/v would have a δ value of about 28.5; such a mixed solvent system is suitable for use herein.

20 It is found that polar solvents capable of forming hydrogen bonding are more effective in lowering the melt viscosity of the composition. As such, a lower amount of the polar solvent is sufficient to adjust the viscosity to the desired range for melt spinning. Using a lower amount of the polar solvent provides a further advantage of reducing the need for an evaporation step during or subsequent to the melt processing step, which results in operating cost advantages such as lower energy
25 consumption, AND lower solvent recovery costs, as well as lower costs for environmental/regulatory compliance.

30 The starch composition may optionally include liquid or volatile processing aids which function mainly as viscosity modifiers of the melt compositions. The processing aid is substantially volatilized and removed during the melt processing stage such that only a residual/trace amount remains in the final product. Thus, they do not adversely affect the strength, modulus or other properties of the final product.

- 18 -

The polar solvents disclosed above may also function as volatile processing aids. Other nonlimiting examples include carbonates such as sodium bicarbonate.

Optionally, other ingredients may be incorporated into the spinnable starch composition to modify the processability and/or to modify physical properties such as elasticity, tensile strength and modulus of the final product. Nonlimiting examples include cross-linking agents, emulsifiers, surfactants, lubricants, other processing aids, optical brighteners, antioxidants, flame retardants, dyes, pigments, fillers, proteins and their alkali salts, biodegradable synthetic polymers, waxes, low melting synthetic thermoplastic polymers, tackifying resins, extenders, and mixtures thereof. These optional ingredients may be present in quantities ranging from 0.1% to 70% by weight of the composition.

Exemplary biodegradable synthetic polymers include polycaprolactone; polyhydroxyalkanoates including polyhydroxybutyrates, and polyhydroxyvalerates; polylactides; and mixtures thereof.

Other additives are typically included with the starch polymer as a processing aid and to modify physical properties such as elasticity, dry tensile strength, and wet strength of the extruded fibers. Additives are typically present in quantities ranging from 0.1% to 70% by weight on a non-volatiles basis. Preferred additives are urea, urea derivatives, cross-linking agents, emulsifiers, surfactants, lubricants, proteins and their alkali salts, biodegradable synthetic polymers, waxes, low melting synthetic thermoplastic polymers, tackifying resins, extenders, and mixtures thereof. Preferred biodegradable synthetic polymers include polycaprolactone, polyhydroxybutyrates, polyhydroxyvalerates, polylactides, and mixtures thereof. Other preferred additives and associated properties include optical brighteners, antioxidants, flame retardants, dyes, pigments, and fillers. For the present invention, a preferred additive is urea in quantities ranging from 20% to 60% by weight.

Suitable extenders for use herein include gelatin, vegetable proteins such as sunflower protein, soybean proteins, cotton seed proteins, and water soluble polysaccharides; such as alginates, carrageenans, guar gum, agar, gum arabic and related gums, pectin, water soluble derivatives of cellulose, such as alkylcelluloses, hydroxyalkylcelluloses, carboxymethylcellulose, etc. Also, water soluble synthetic

- 19 -

polymers, such as polyacrylic acids, polyacrylic acid esters, polyvinylacetates, polyvinylalcohols, polyvinylpyrrolidone, etc., may be used.

Lubricant compounds may further be added to improve the flow properties of the starch material during the processes used for producing the present invention. The lubricant compounds can include animal or vegetable fats, preferably in their hydrogenated form, especially those which are solid at room temperature. Additional lubricant materials include mono-glycerides and di-glycerides and phosphatides, especially lecithin. For the present invention, a preferred lubricant compound includes the mono-glyceride, glycerol mono-stearate.

Further additives including inorganic fillers such as the oxides of magnesium, aluminum, silicon, and titanium may be added as inexpensive fillers or processing aides. Additionally, inorganic salts, including alkali metal salts, alkaline earth metal salts, phosphate salts, etc., may be used as processing aides.

Other additives may be desirable depending upon the particular end use of the product contemplated. For example, in products such as toilet tissue, disposable towels, facial tissues and other similar products, wet strength is a desirable attribute. Thus, it is often desirable to add to the starch polymer cross-linking agents known in the art as "wet strength" resins.

A general dissertation on the types of wet strength resins utilized in the paper art can be found in TAPPI monograph series No. 29, Wet Strength in Paper and Paperboard, Technical Association of the Pulp and Paper Industry (New York, 1965). The most useful wet strength resins have generally been cationic in character. Polyamide-epichlorohydrin resins are cationic polyamide amine-epichlorohydrin wet strength resins which have been found to be of particular utility. Suitable types of such resins are described in U.S. Patent Nos. 3,700,623, issued on October 24, 1972, and 3,772,076, issued on November 13, 1973, both issued to Keim and both being hereby incorporated by reference. One commercial source of a useful polyamide-epichlorohydrin resin is Hercules, Inc. of Wilmington, Delaware, which markets such resins under the mark Kymene®.

Glyoxylated polyacrylamide resins have also been found to be of utility as wet strength resins. These resins are described in U.S. Patent Nos. 3,556,932,

- 20 -

issued on January 19, 1971, to Coscia, et al. and 3,556,933, issued on January 19, 1971, to Williams et al., both patents being incorporated herein by reference. One commercial source of glyoxylated polyacrylamide resins is Cytec Co. of Stanford, CT, which markets one such resin under the mark Parex[®] 631 NC.

5 It is found that when suitable cross-linking agent such as Parex[®] is added to the starch composition of the present invention under acidic condition, The composition is rendered water insoluble. That is, the water solubility of the composition, as tested by the Test Method described hereinafter, is less than 30%, preferably less than 20%, more preferably less than 10% and most preferably less than 10 5%. The products such as fibers and films made from such a composition are also water insoluble.

Still other water-soluble cationic resins finding utility in this invention are urea formaldehyde and melamine formaldehyde resins. The more common functional groups of these polyfunctional resins are nitrogen containing groups such as 15 amino groups and methylol groups attached to nitrogen. Polyethylenimine type resins may also find utility in the present invention. In addition, temporary wet strength resins such as Caldas[®] 10 (manufactured by Japan Carlit) and CoBond[®] 1000 (manufactured by National Starch and Chemical Company) may be used in the present invention.

20 For the present invention, a suitable cross-linking agent is added to the composition in quantities ranging from about 0.1% by weight to about 10% by weight, more preferably from about 0.1% by weight to about 3% by weight.

The Rheology of The Starch Compositions

25 The rheological behavior of the starch composition is an important consideration for selecting suitable materials and fabrication equipment/processes. Many factors contribute to the rheological behavior of the starch composition, including the amount and the type of polymeric components used, the molecular weight and molecular weight distribution of the components, the amount and type of additives (e.g., plasticizers, processing aids), the processing conditions such as 30 temperature, pressure, rate of deformation, and relative humidity, and in the case of non-Newtonian materials, the deformation history (i.e., a time or strain history

- 21 -

dependence).

The starch composition of the present invention typically has a high solid content (i.e., a concentration above a critical concentration C^*) such that a dynamic or fluctuating entangled network is formed wherein the starch molecules and the high polymers become associated and disassociated temporally. The association may be in the form of physical entanglements, van der Waals forces, or chemical interactions such as hydrogen bonding. The starch composition having the entangled network structure exhibits melt flow behavior typical of a non-Newtonian fluid.

The starch composition of the present invention may exhibit a strain hardening behavior, that is, the extensional viscosity increases as the strain or deformation increases. Typically, a Newtonian fluid exhibit a linear relationship between stress/force and strain. That is, there is no strain hardening behavior in a Newtonian fluid. On the other hand, a non-Newtonian fluid may exhibiting an increase in force at higher strain (i.e, strain hardening) while still exhibit a linear force - strain relationship at lower strain (i.e, Newtonian-like).

The strain experienced by a fluid element in a non-Newtonian fluid is dependent on its kinematic history, that is

$$\epsilon = \int_0^t \dot{\epsilon}(t') dt'$$

This time or history dependent strain is called the Hencky strain (ϵ_H). For an ideal homogeneous uniaxial elongation, the strain rate experienced by every fluid element is equal to the strain imposed by the applied stress, such as the stresses applied externally by the instrument, device or process. In such an ideal case, the Hencky strain correlates directly with the sample deformation/elongation

$$\epsilon_H = \ln (L/L_0)$$

Such an ideal strain response to applied stress is most often observed in Newtonian fluids.

The Trouton ratio (Tr) is often used to express the extensional flow behavior. The Trouton ratio is defined as the ratio between the extensional viscosity (η_e) and the shear viscosity (η_s),

- 22 -

$$Tr = \eta_e(\dot{\epsilon}, t) / \eta_s$$

wherein the extensional viscosity η_e is dependent on the deformation rate ($\dot{\epsilon}$) and time (t). For a Newtonian fluid, the uniaxial extension Trouton ratio has a constant value of 3. For a non-Newtonian fluid, the extensional viscosity is dependent on the deformation rate ($\dot{\epsilon}$) and time (t).

Shear viscosity (η_s) relates to the melt processability of the starch composition using standard polymer processing techniques, such as extrusion, blow molding, compression molding, injection molding and the like. A starch composition having a shear viscosity, measured according to the Test Method disclosed hereinafter, of less than about 30 Pa•s, preferably from about 0.1 to about 10 Pa•s, more preferably from about 1 to about 8 Pa•s, is useful in the melt attenuation processes herein. Some starch compositions herein may have low melt viscosity such that they may be mixed, conveyed, or otherwise processed in traditional polymer processing equipment typically used for viscous fluids, such as a stationary mixer equipped with metering pump and spinneret. The shear viscosity of the starch composition may be effectively modified by the molecular weight and molecular weight distribution of the starch, the molecular weight of the high polymer, and the amount of plasticizers and/or solvents used. It is found that reducing the average molecular weight of the starch is an effective way to lower the shear viscosity of the composition.

It is generally known that melt shear viscosity is a material property useful for evaluating melt processability of the material in traditional thermoplastic processes such as injection molding or extrusion. For conventional fiber spinning thermoplastics such as polyolefins, polyamides and polyesters, there is a strong correlation between shear viscosity and extensional viscosity of these conventional thermoplastic materials and blends thereof. That is, the spinnability of the material can be determined simply by the melt shear viscosity, even though the spinnability is a property controlled primarily by melt extensional viscosity. The correlation is quite robust such that the fiber industry has relied on the melt shear viscosity in selecting and formulating melt spinnable materials. The melt extensional viscosity has rarely been used as an industrial screening tool.

It is therefore surprising to find that the starch compositions of the

- 23 -

present invention do not exhibit such a correlation between shear and extensional viscosities. Specifically, when a high polymer selected according to the present invention is added to a starch composition, the shear viscosity of the composition remains relatively unchanged, or even decreases slightly. Based on conventional wisdom, such a starch composition would exhibit decreased melt processability and would not be suitable for melt extensional processes. However, it is surprisingly found that the starch composition herein shows a significant increase in extensional viscosity when even a small amount of high polymer is added. Consequently, the starch composition herein is found to have enhanced melt extensibility and is suitable for melt extensional processes (e.g., blow molding, spun bonding, blown film molding, foam molding, and the like).

Extensional or elongational viscosity (η_e) relates to melt extensibility of the composition, and is particularly important for extensional processes such as fiber, film or foam making. The extensional viscosity includes three types of deformation: uniaxial or simple extensional viscosity, biaxial extensional viscosity, and pure shear extensional viscosity. The uniaxial extensional viscosity is important for uniaxial extensional processes such as fiber spinning, melt blowing, and spun bonding. The other two extensional viscosities are important for the biaxial extension or forming processes for making films, foams, sheets or parts. It is found that the properties of the high polymers have a significant effect on melt extensional viscosity. The high polymers useful for enhancing the melt extensibility of the starch composition of the present invention are typically high molecular weight, substantially linear polymers. Moreover, high polymers that are substantially compatible with starch are most effective in enhancing the melt extensibility of the starch composition.

It has been found that starch compositions useful for melt extensional processes typically have their extensional viscosity increased by a factor of at least 10 when a selected high polymer is added to the composition. Typically, the starch compositions of present invention show an increase in the extensional viscosity of about 10 to about 500, preferably of about 20 to about 300, more preferably from about 30 to about 100, when a selected high polymer is added.

It has also been found that melt processable compositions of the present

- 24 -

invention typically have a Trouton ratio of at least about 3. Typically, the Trouton ratio ranges from about 10 to about 5,000, preferably from about 20 to about 1,000, more preferably from about 30 to about 500, when measured at 90 °C and 700 s⁻¹.

When the starch composition of the present composition is subjected to an uniaxial extensional process, a draw ratio, expressed in (D_0^2/D^2) wherein D_0 is the diameter of filament before drawing and D is the diameter of the drawn fiber, greater than 1000 can be easily achieved. The starch composition of the present invention typically achieves a draw ratio from about 100 to about 10,000, preferably greater than about 1,000, more preferably greater than about 3,000 and most preferably greater than about 5,000. More specifically, the starch composition of the present invention has sufficient melt extensibility to be melt drawn to fine fibers having a finite average diameter of less than 50 microns, preferably less than 25 microns, more preferably less than 15 microns, even more preferably less than 10 microns, and most preferably less than 5 microns.

When the starch composition of the present invention is subjected to a biaxial extensional process, the enhanced melt extensibility of the composition allows it to be melt drawn to films having a finite average caliper of less than 0.8 mils, preferably less than 0.6 mils, more preferably less than 0.4 mils, even more preferably less than 0.2 mils, and most preferably less than 0.1 mils.

The starch composition herein is processed in a flowable state, which typically occurs at a temperature at least equal to or higher than its melting temperature. Therefore, the processing temperature range is controlled by the melting temperature of the starch composition, which is measured according to the Test Method described in detail herein. The melting temperature of the starch composition herein ranges from about 80 to 180°C, preferably from about 85 to about 160°C, and more preferably from about 90 to about 140°C. It is to be understood that some starch compositions may not exhibit pure "melting" behavior. As used herein, the term "melting temperature" means the temperature or the range of temperature at or above which the composition melts or softens.

Exemplary uniaxial extensional processes suitable for the starch compositions include melt spinning, melt blowing, and spun bonding. These processes

- 25 -

are described in detail in U. S. Patent No. 4,064,605, issued on December 27, 1977 to Akiyama et al.; U.S. Patent No. 4,418,026, issued on November 29, 1983 to Blackie et al.; U. S. Patent No. 4,855,179, issued on August 8, 1989 to Bourland et al.; U. S. Patent No. 4,909,976, issued on March 20, 1990 to Cuculo et al.; U. S. Patent No. 5,145,631, issued on September 8, 1992 to Jezic; U.S. Patent No. 5,516,815, issued on May 14, 1996 to Buehler et al.; and U.S. Patent No. 5,342,335, issued on August 30, 1994 to Rhim et al.; the disclosure of all of the above are incorporated herein by reference. The resultant products may find use in filters for air, oil and water; vacuum cleaner filters; furnace filters; face masks; coffee filters, tea or coffee bags; thermal insulation materials and sound insulation materials; nonwovens for one-time use sanitary products such as diapers, feminine pads, and incontinence articles; biodegradable textile fabrics for improved moisture absorption and softness of wear such as microfiber or breathable fabrics; an electrostatically charged, structured web for collecting and removing dust; reinforcements and webs for hard grades of paper, such as wrapping paper, writing paper, newsprint, corrugated paper board, and webs for tissue grades of paper such as toilet paper, paper towel, napkins and facial tissue; medical uses such as surgical drapes, wound dressing, bandages, dermal patches and self-dissolving sutures; and dental uses such as dental floss and toothbrush bristles. The fibrous web may also include odor absorbants, termite repellants, insecticides, rodenticides, and the like, for specific uses. The resultant product absorbs water and oil and may find use in oil or water spill clean-up, or controlled water retention and release for agricultural or horticultural applications. The resultant starch fibers or fiber webs may also be incorporated into other materials such as saw dust, wood pulp, plastics, and concrete, to form composite materials, which can be used as building materials such as walls, support beams, pressed boards, dry walls and backings, and ceiling tiles; other medical uses such as casts, splints, and tongue depressors; and in fireplace logs for decorative and/or burning purpose.

The melt rheological behavior of the present starch composition also makes it suitable for use in conventional thermoplastic processes that involves biaxial extension of the material. By having the proper melt shear viscosity and biaxial extensional viscosity, the starch compositions of the present invention may

- 26 -

substantially reduce the occurrence of tearing, surface defects, and other breakdowns or defects that interrupt continuous processes and produce unsatisfactory products. These processes include blow molding, blown film extrusion or coextrusion, vacuum forming, pressure forming, compression molding, transfer molding and injection molding. Nonlimiting examples of these processes are described in details in U.S. Patent No. 5,405,564, issued on April 11, 1995 to Stepto et al.; U.S. Patent No. 5,468,444, issued on November 21, 1995 to Yazaki et al.; U.S. Patent No. 5,462,982, issued on October 31, 1995 to Bastioli et al.; the disclosure of all of the above are hereby incorporated by reference. The articles produced by these processes include sheets, films, coatings, laminates, pipes, rods, bags, and shaped articles (such as bottles, containers). The articles may find use as bags such as shopping bags, grocery bags, and garbage bags; pouches for food storage or cooking; microwavable containers for frozen food; and pharmaceutical uses such as capsules or coatings for medicine. The films may be substantially transparent for use as food wraps, shrink wraps or windowed envelopes. The films may also be further processed for use as an inexpensive, biodegradable carrier for other materials such as seeds or fertilizers. Adhesives may be applied to the films or sheets for other uses such as labels.

The starch compositions of the present invention may also be made into a foamed structure by controlled removal of the volatile components (e.g., water, polar solvents). However, foaming or expanding agents are generally incorporated to produce articles having foamed or porous internal structure. Exemplary foaming or expanding agents include carbon dioxide, n-pentane, and carbonate salts such as sodium bicarbonate, either alone or in combination with a polymeric acid which has lateral carboxyl groups (e.g., polyacrylic acid, ethylene-acrylic copolymer).

Nonlimiting examples of the foaming and forming processes are described in U. S. Patent No. 5,288,765, issued on February 22, 1994 to Bastioli et al.; U.S. Patent No. 5,496,895, issued on March 5, 1996 to Chinnaswamy et al.; U.S. Patent No. 5,705,536, issued on January 6, 1998 to Tomka; and U.S. Patent No. 5,736,586, issued on April 7, 1998 to Bastioli et al.; the disclosures of which are hereby incorporated by reference. The resultant products may find use in egg cartons; foamed cups for hot beverages; containers for fast food; meat trays; plates and bowls for one-time use such as at picnic

- 27 -

or parties; packaging materials, either loose-fill or molded to conform to the packed article (e.g., a computer shipping package); thermal insulation materials; and noise insulation or sound proofing materials.

(2) Exemplary Processes

5

Extruder Apparatus

The apparatus for carrying out the process of the invention consists of an extruder having

- a. first inlet chamber containing at least one conveying element,
- b. a heated receiving chamber downstream of said first chamber and
- 10 containing at least one conveying element;
- c. a heated destructurization chamber, downstream of said second chamber, containing kneading and retaining elements;
- d. a heated degassing chamber under reduced pressure downstream of said destructurization chamber and said degassing chamber containing at least one
- 15 conveying element, and
- e. a heated extrusion chamber downstream of said degassing chamber being under elevated pressure and having at least one conveying element.

Furthermore, the extruder preferably has at least one delivery device for solids for process step a, a liquid metering device for process step b, a degassing

20 fitting for process step d, and a die for process step e. A twin screw extruder having closely meshing screws which run in the same direction is preferred.

For the present invention, the starch material can have a total water content, i.e. water of hydration plus added water, in the range of about 5 to about 40%; preferably in the range of about 10 to about 20%. The starch material is heated to

25 elevated temperatures sufficient to form a pseudo-thermoplastic melt. Such temperature is typically higher than the glass transition and/or melting temperature of the formed material. For the present invention, the glass transition temperatures are at least about minus -30°C, preferably in the range of about -30°C to about 150°C, more preferably in the range of about -30°C to about 100°C, and most preferably in the

30 range of about -30°C to about 25°C. The melting temperature is preferably in the range of about 100°C to about 180°C. The pseudo-thermoplastic melts of the

- 28 -

invention are polymeric fluids having a shear rate dependent viscosity, as known in the art. The viscosity decreases with increasing shear rate as well as with increasing temperature.

The starch material is heated preferably in a closed volume in the presence of a low concentration of water to convert the starch material to a pseudo-thermoplastic melt. A closed volume can be a closed vessel or the volume created by the sealing action of the feed material as happens in the screw of extrusion equipment. Pressures created in a closed vessel will include pressures due to the vapor pressure of water as well as pressures generated due to compression of materials in the screw-barrel of the extruder.

A chain scission catalyst, which reduces the molecular weight by splitting the glycosidic bonds in the starch macromolecules resulting in a reduction of the average molecular weight of the starch, may be used to reduce the viscosity of the pseudo-thermoplastic melt. Suitable catalysts include inorganic and organic acids. Suitable inorganic acids include hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, and boric acid as well as the partial salts of polybasic acids, e.g. NaHSO_4 or NaH_2PO_4 etc. Suitable organic acids include formic acid, acetic acid, propionic acid, butyric acid, lactic acid, glycolic acid, oxalic acid, citric acid, tartaric acid, itaconic acid, succinic acid, and other organic acids known in the art, including partial salts of the polybasic acids. For the present invention, the preferred catalysts are hydrochloric acid, sulfuric acid, and citric acid, including mixtures thereof.

The reduction of the molecular weight of the non-modified starch used is by a factor of 2 to 5000, preferably by a factor of 4 to 4000. The concentration of catalysts is in the range of 10^{-6} to 10^{-2} mole of catalyst per mole of anhydro-glucose unit, preferably between 0.1×10^{-3} to 5×10^{-3} mole of catalyst per mole of anhydro-glucose unit of starch.

The following examples illustrate the type of extrusion equipment and operating parameters for producing starch fibers.

EXAMPLE 1

The purpose of this example is to illustrate starch fibers extruded at a particular cross section and subsequently drawn to a reduced cross section. Drawn

- 29 -

pseudo-thermoplastic starch fibers were produced using a torque rheometer assembly 100 illustrated in Figure 1a. The torque rheometer assembly 100 includes a drive unit 110 (manufactured by Haake GmbH, model Rheocord 90), a barrel 120 partitioned into four temperature zones 122, 124, 126 and 128, a feed port 121, a single capillary die 130, and a simple mandrel winder 140. Twin screw elements 160 (model TW100, from Haake GmbH), depicted in Figure 1b, are attached to the drive unit 110 and disposed within the barrel 120. A capillary die was made to fit the die 130, with an orifice diameter of 0.5 mm and a length of 5.6 mm. The mandrel rewinder 140 comprises a 3 inch core mounted to a simple DC driven 3 inch diameter shaft. The 3 inch core can achieve surface speeds from 150 to 2000 fpm.

Raw materials utilized included the following:

45% by weight Durabond A Corn Starch from National Starch

25% by weight Water

15% by weight Urea available from Aldrich Chemicals

15% by weight Sorbitol available from Aldrich Chemicals

All raw materials were mixed off-line until a slurry was formed. The slurry was then manually fed into the feed port 121 of the torque rheometer assembly 100.

The settings on the torque rheometer were as follows:

RPM	50
Barrel Temperature	110 °C
Die Temperature	105 °C
Feed Rate	1.7 grams/minute

After running the rheometer for approximately 20 minutes, the process stabilized and a single pseudo-thermoplastic starch fiber 150 exited the die 130. The single fiber 150 was manually wound around the mandrel winder 140. The winder 140 was then slowly sped up to 900 feet/minute surface speed in order to draw the fiber 150 increasing the fiber length and decreasing the cross sectional area. The diameter of the wound fiber 150 was between 70 and 90 microns.

EXAMPLE 2

The purpose of this example is to illustrate how starch fibers can be arranged to

- 30 -

form a starch fiber structure. The pseudo-thermoplastic starch fibers of Example 1 were cut into 8 mm length staple fibers. The starch staple fibers at a basis weight of 55 g/m² were air laid onto a papermaking forming fabric as described in U.S. Patent No. 4,637,859, with the fabrics of U.S. Patent Nos. 5,857,498, 5,672,248, 5,211,815 and 5,098,519, all incorporated herein by reference, also being judged suitable for this purpose. The fibers were misted with water at a level of 20%, based on the weight of the fibers, and then dried at an elevated temperature to produce a bonded starch fiber structure.

EXAMPLE 3

STARCH FIBERS EXTRUDED USING A VENTED TWIN SCREW EXTRUDER

The purpose of this example is to illustrate a vented twin screw extruder configuration, depicted in Figure 2a, used to make starch fibers for the present invention. Starch fibers are made using a an APV Baker (Peterborough, England) twin screw extruder 200, a capillary die 212, and a winder (not shown).

As show in Figure 2a, the twin screw extruder comprises a barrel 202 that is separated into five zones. The barrel 202 encloses the extrusion screws and mixing elements and serves as a containment vessel during the extrusion process. A solid feed port 204 is disposed in zone 1 and liquid feed ports 206 and 208 are disposed in zone 1 and zone 2. A vent 210 is included in zone 4 for venting the pseudo-thermoplastic melt to decrease the water content of the mixture prior to extrusion through the die 212.

The screw and mixing element configuration 300 for the twin screw extruder 200 is illustrated in Figure 2b. The twin screw extruder comprises a plurality of twin lead screws (TLS) and single lead screws (SLS) installed in series. Screw elements are characterized by the number of continuous leads and the pitch of these leads.

A lead is a flight (at a given helix angle) which wraps the core of the screw element. The number of leads indicates the number of flights wrapping the core at any given location along the length of the screw. Increasing the number of leads reduces the volumetric capacity of the screw and increase the pressure generating capability of the screw.

- 31 -

The pitch of the screw is the distance needed for a flight to complete one revolution of the core. It is expressed as the number of screw element diameters per one complete revolution of a flight. Decreasing the pitch of the screw increase the pressure generated by the screw and decreases the volumetric capacity of the screw.

5 The length of a screw element is reported as the ratio of length of the element divided by the diameter of the element.

This example uses TLS and SLS. Screw element 310 is a TLS with a 1.0 pitch and a 1.5 length ratio. Screw element 320 is a TLS with a 1.0 pitch and a 1.0 L/D ratio. Screw element 340 is a SLS with a $\frac{1}{4}$ pitch and a 1.0 length ratio. Screw
10 element 350 is a SLS and a $\frac{1}{4}$ pitch and a $\frac{1}{2}$ length ratio.

Bilobal paddles 360 serving as mixing elements are also included in a series with the SLFS and TLFS screws in order to enhance mixing. Various configurations of bilobal paddles 360 and reversing elements 340 and 350 are used in order to control flow and corresponding mixing time.

15 In zone 1, Durabond A starch and sorbitol are fed into the solid feed port 204 and urea is fed into the liquid port 208 forming a mixture with a 60/20/20 weight ratio. These materials are combined inside the extruder with water added at the liquid feed port 206 to form a pseudo-thermoplastic melt. The temperature, pressure, and
20 corresponding function of each zone are provided in Table I.

Table I

Zone	Temperature (deg F)	Pressure (gauge PSI)	Description of Screw
1	70	0	Feeding
2	193	34	Mixing
3	268	0	Mixing
4	210	0	Pressure Decreasing Conveying
5	205	0-10	Pressure Generating
Die	194	430	Shaping

- 32 -

EXAMPLE 4STARCH FIBERS EXTRUDED WITH A NON-VENTED TWIN SCREW
EXTRUDER

The purpose of this example is to illustrate a non-vented twin screw extruder configuration, depicted in Figure 3a, used to make starch fibers for the present invention. Starch fibers are made using an APV Baker (Peterborough, England) twin screw extruder 200, a capillary die 212, and a winder (not shown).

The non-vented twin screw extruder configuration is illustrated in Figure 3a. The twin screw extruder comprises a barrel 202 that is separated into five zones. The barrel 202 encloses the extrusion screws and mixing elements and serves as a containment vessel during the extrusion process. A solid feed port 204 is disposed in zone 1 and liquid feed ports 206, and 208 are disposed in zone 1 and zone 2.

The screw and mixing element configuration for the twin screw extruder is illustrated in Figure 3b.

In zone 1, Durabond A starch and sorbitol are fed into the solid feed port 204 and urea is fed into the liquid port 208 forming a mixture with a 60/20/20 weight ratio. These materials are combined inside the extruder with water added at the liquid feed port 206 to form a pseudo-thermoplastic melt. The temperature, pressure, and corresponding function of each zone are provided in Table II.

Table II

Zone	Temperature (deg F)	Pressure (gauge PSI)	Description of Screw
1	70	0	Feeding
2	180	0	Mixing
3	260	0	Mixing
4	215	0	Pressure Decreasing Conveying
5	193	30	Pressure Generating
Die	172	150	Shaping

- 33 -

EXAMPLE 5FOAMED STARCH FIBERS EXTRUDED WITH A NON-VENTED TWIN
SCREW EXTRUDER

The purpose of this example is to illustrate the various zones of a twin screw extruder without a vent and the operating parameters associated with each zone for producing foamed starch fibers which are lower in density and having a higher absorbent capacity relative to non-foamed starch fibers. Foamed starch fibers are made using a fiber making apparatus comprising the twin screw extruder configuration depicted in Figures 3a and 3b.

In zone 1, Durabond A starch and sorbitol are fed into the solid feed port 204 and urea is fed into the liquid port 208 forming a mixture with a 60/20/20 weight ratio. These materials are combined inside the extruder with water added at the liquid feed port 206 to form a pseudo-thermoplastic melt. The temperature, pressure, and corresponding function of each zone are provided in Table III.

TABLE III

Zone	Temperature (deg F)	Pressure (gauge PSI)	Description of Screw
1	70	0	Feeding
2	180	0	Mixing
3	260	0	Mixing
4	240	0	Pressure Decreasing Conveying
5	220	30	Pressure Generating
Die	225	150	Shaping

Pseudo-thermoplastic Starch Melt Fiber Spinning

The production of fibers according to the invention from the pseudo-thermoplastic melt compositions occurs by the usual melt spinning processes. Devices for producing non-woven thermoplastic fabric structures from extruded polymers are well known in the art. Extruded polymers under pressure, are forced through a spinneret forming a vertically oriented curtain of downward advancing fibers. The fibers are quenched with air in conjunction with a suction-type drawing or attenuating air slot. U.S. Pat. No. 5,292,239 issued to Zeldin, et al., March 8, 1994, discloses a device that reduces significant turbulence in the air flow in order to uniformly and

- 34 -

consistently apply a drawing force to the fibers.

For the present invention, structures are produced from a mixture comprising starch, water, plasticizers, and other optional additives. As shown in Figure 4, the mixture is converted to a pseudo-thermoplastic melt in an extruder and conveyed through a spinneret 10 to a drawing unit 20 forming a vertically oriented curtain of downward advancing fibers F.

The spinneret 10 comprises an assembly which is known in the art. The spinneret 10 includes a plurality of nozzle bores 12 with hole diameters customary for fiber production. The spinneret assembly 10 can be adapted to the fluidity of the melt so that every nozzle bore 12 has the same rate of flow.

The drawing unit 20 comprises an open upper end 22, an open lower end 24, and an air supply manifold 26 supplying compressed air to internal nozzles (not shown) oriented in a downward direction. As compressed air flows through the internal nozzles, air is drawn into the open upper end 22 of the drawing unit 20 forming a rapidly moving stream of air flowing in the downward direction. The air stream produces a drawing force on the fibers causing them to be attenuated or stretched before exiting the open lower end 24 of the drawing unit 20.

For the present invention, the fibers exiting the drawing unit 20 can have a size ranging from about 0.01 decitex to about 135 decitex. Preferably, the fibers exiting the drawing unit 20 have a size ranging from about 0.02 decitex to about 30 decitex. Most preferably, the fibers exiting the drawing unit 20 have a size ranging from about 0.02 decitex to about 5 decitex.

Upon exiting the drawing unit 20, the fibers are deposited on a moving conveyor belt 30 to form flexible, low density structure comprising fibers. The fibers are then joined to each other through conventional techniques. A preferred process for producing structures of the present invention is described in U.S. Pat. No. 5,688,468 issued to Lu, November 18, 1997, which is incorporated herein by reference.

In addition to spunbonded structures, mono-fibers, multi-fibers, staple fibers, hollow fibers, shaped fibers, such as multi-lobal fibers and multi-component fibers can all be produced by using the compositions and methods of the present invention. The process for the production of these fibers may be in one stage with a

- 36 -

immersed in water for five seconds. The method used to determine this measure is described below. For the present invention, the structure comprising pseudo-thermoplastic starch fibers can have a GMWT ranging from about 2 g/cm to about 400 g/cm. More preferably, the structure can have a GMWT ranging from about 2 g/cm to about 200 g/cm.

Geometric mean decayed wet tensile strength (GMDWT) is a measure of the wet tensile strength of the structure after being immersed in water for thirty minutes. For the present invention, the structure comprising pseudo-thermoplastic starch fibers can have a GMDWT ranging from about 0 g/cm to about 20 g/cm. More preferably, the structure can have a GMDWT ranging from about 0 g/cm to about 10 g/cm.

Softness has been described as a physiologically perceived attribute which is generally measured by expert or non-expert panel evaluations. Perceived softness can be broken down into two components; bulk softness and surface softness. Bulk softness has been correlated to sheet stiffness and flexibility while surface softness has been related to surface texture and smoothness. High softness requires flexibility. The method used for determining the total flexibility of a structure is defined below. For the present invention, the structure has a total flexibility ranging from about 1.0 g/cm to about 75 g/cm; preferably from about 2.0 g/cm to about 50 g/cm; and more preferably from about 2.0 g/cm to about 35 g/cm.

Products such as disposable towels, toilet tissue, facial tissue, napkins, and wet wipes require a certain level of absorbency. Herein, absorbency means absorbent capacity which is a measure of the amount of distilled water absorbed and retained by the structure. The method used for determining the absorbency of a structure is defined below. For the present invention, the structure has an absorbency ranging from about

1 $\frac{g_{\text{Water}}}{g_{\text{Dry Structure}}}$ to

about 15 $\frac{g_{\text{Water}}}{g_{\text{Dry Structure}}}$; preferably from about 2 $\frac{g_{\text{Water}}}{g_{\text{Dry Structure}}}$ to about 14 $\frac{g_{\text{Water}}}{g_{\text{Dry Structure}}}$; more preferably from about 3 $\frac{g_{\text{Water}}}{g_{\text{Dry Structure}}}$ to about 13 $\frac{g_{\text{Water}}}{g_{\text{Dry Structure}}}$.

(4) ANALYTICAL METHODS

(a) Sample Conditioning And Preparation:

Prior to testing, samples are conditioned at a relative humidity of 48% to 50% and within a temperature range of 22°C to 24°C until a moisture content of from about 5% to about 16% by weight as measured by TGA (Thermo Gravimetric Analysis) is achieved. For Thermo Gravimetric Analysis, a Hi-res. TGA2950 Termogravimetric analyzer from TA Instruments is used. Approximately 20 mg of sample is weighed into a TGA pan. Following the manufacturer's instructions, the sample and pan are inserted into the unit and the temperature is increased at a rate of 10°C/minute to 250°C. The % moisture in the sample is determined using the weight lost and the initial weight as follows:

$$\% \text{ Moisture} = \frac{\text{Start Weight} - \text{Weight @ } 250^{\circ}\text{C}}{\text{Start Weight}} \cdot 100\%$$

where all weights are in milligrams.

(b) Basis Weight

One stack of 8 plies is made from the preconditioned samples. The stack of 8 plies is cut into a 4 inch by 4 inch square. A rule die from Acme Steel Rule Die Corp. (5 Stevens St. Waterbury Conn., 06714) is used to accomplish this cutting. For the actual measurement of the weight of the sample, a top loading balance with a minimum of 0.01 g readability is used. The stack of 8 plies is laid on the pan of the top loading balance. The balance is protected from air drafts and other disturbances using a draft shield. Weights are recorded when the readings on the balance become constant. Weights are measured in grams.

The weight reading is divided by the number of plies tested. The weight reading is also divided the weight reading by the area of the sample which is normally 16 square inches, which is approximately equal to 0.0103 square meters. The unit of measure for basis weight as used herein is grams/square meter. This is calculated using the 0.0103 square meter area noted above.

(c) Caliper

Preconditioned samples are cut to a size greater than the size of the foot used to measure the caliper. The foot to be used is a circle with an area of 3.14 square inches.

- 38 -

The sample is placed on a horizontal flat surface and confined between the flat surface and a load foot having a horizontal loading surface, where the load foot loading surface has a circular surface area of about 3.14 square inches and applies a confining pressure of about 15 g/square cm (0.21 psi) to the sample. The caliper is the resulting gap between the flat surface and the load foot loading surface. Such measurements can be obtained on a VIR Electronic Thickness Tester Model II available from Thwing-Albert, Philadelphia, Pa. The caliper measurement is repeated and recorded at least five times. The result is reported in millimeters.

The sum of the readings recorded from the caliper tests is divided by the number of readings recorded. The result is reported in millimeters (mm).

(d) Dry Tensile Strength

The dry tensile strength is determined on one inch wide strips of sample using a Thwing-Albert Intellect II Standard Tensile Tester (Thwing-Albert Instrument Co., 10960 Dutton Rd., Philadelphia, Pa., 19154). This method is intended for use on finished paper products, reel samples, and unconverted stocks.

Two stacks of 8 plies are made from the preconditioned samples. From one of these stacks of 8 plies, four strips are cut 1 inch by 7 inch with the long 7 inch dimension running parallel to the machine direction. Note these samples are machine direction samples. An additional four strips 1 inch by 7 inch with the long 7 inch dimension running parallel to the cross direction. All cuts are made using a cutter (JDC-1-10 or JDC-1-12 with safety shield from Thwing-Albert Instrument Co., 10960 Dutton Road, Philadelphia, Pa., 19154). A total of eight samples are produced: four 1 inch by 7 inch strips, 8 plies thick, with the 7 inch dimension running parallel to the machine direction and four 1 inch by 7 inch strips, 8 plies thick, with the 7 inch dimension running parallel to the cross direction.

Each of the four eight ply stacks of machine direction and cross machine direction sample tensile strips are measured in the Thwing-Albert Intellect II Standard Tensile Tester. The four measurements of the 8 ply stacks of machine direction sample tensile strips are summed and divided by four, which is the number of machine direction strips tested. The sum is also divided by eight, which the number of usable units per tensile strip. The calculation is repeated for the cross machine

- 39 -

direction measurements.

All results are in units of grams/inch. Appropriate unit conversions may be made to achieve units of grams/cm as reported herein.

(e) Initial Wet Tensile Strength

5 For the initial wet tensile strength determination, a portion of the test sample is immersed in water for five seconds prior to the tensile strength measurement. The wet tensile strength is determined on one inch wide strips of sample using a Thwing-Albert Intelect II Standard Tensile Tester (Thwing-Albert Instrument Co., 10960 Dutton Rd., Philadelphia, Pa., 19154) and a Finch Wet Strength Device,
10 Catalog Number 731D (Thwing-Albert Instrument Co., 10960 Dutton Rd., Philadelphia, Pa., 19154).

15 Prior to sample preparation and wet tensile testing, the samples should be cured in a forced draft oven at 105 ± 3 degree Celsius for a period of 5 minutes ± 10 seconds. The samples should be suspended in the oven such that the forced air can circulate between them.

20 Sample preparation and all aspects of the wet tensile testing should take place within the confines of the constant temperature and humidity room. Two stacks of 5 plies each are made from the cured samples after conditioning. From one of these stacks of 5 plies, four strips are cut 1 inch by 4 inch with the long 4 inch dimension running parallel to the machine direction for machine direction samples. An additional four strips are cut 1 inch by 4 inch with the long 4 inch dimension running parallel to the cross direction for cross direction samples. All cuts are made using a paper cutter (JDC-1-10 or JDC-1-12 with safety shield from Thwing-Albert Instrument Co., 10960 Dutton Road, Philadelphia, Pa., 19154). There are a total of eight samples: four 1 inch
25 by 4 inch strips which are 5 plies thick with the 4 inch dimension running parallel to the machine direction and four 1 inch by 4 inch strips which are 5 plies thick with the 4 inch dimension running parallel to the cross direction.

30 Each of the four five ply stacks of machine direction and cross machine direction sample tensile strips are measured in the Thwing-Albert Intelect II Standard Tensile Tester. The four measurements of the 5 ply stacks of machine direction sample tensile strips are summed and divided by four, which is the number of machine

- 40 -

direction strips tested. The sum is also divided by five, which the number of usable units per tensile strip. The calculation is repeated for the cross machine direction measurements.

5 All results are in units of grams/inch. Appropriate unit conversions may be made to achieve units of grams/cm as reported herein.

(f) Decayed Wet Tensile (Soaked for 30 minutes)

Same as the Initial Wet Tensile Strength except the samples are allowed to soak in the water for 30 minutes (± 30 seconds) prior to Wet Tensile Strength Testing.

10 (g) Flexibility

Flexibility as used herein is defined as the slope of the secant of the graph-curve derived from force vs. stretch % data which secant passes through the origin (zero % stretch, zero force) and through the point on the graph-curve where the force per centimeter of width is 20 grams. For example, for a sample which stretches 15 10% (i.e., 0.1 cm/cm of length) with 20 grams of force per cm of sample width, the slope of the secant through (0%, 0) and (10%, 20) is 2.0 using the formula:

$$\text{Slope} = \frac{Y_2 - Y_1}{X_2 - X_1}$$

20 Total Flexibility as used herein means the geometric mean of the machine-direction flexibility and cross-machine-direction flexibility. Mathematically, this is the square root of the product of the machine-direction flexibility and cross-machine-direction flexibility in grams per cm.

(h) Absorbency

25 Absorbency herein is defined as the amount (grams) of distilled water at 73 ± 2 °F per gram of sample held by the sample after it has been submerged in a water bath for a period of 30 ± 3 seconds and then allowed to sit in a horizontal position for 120 ± 5 seconds followed by 60 ± 5 seconds sitting at a 75° angle (as measured off of horizontal).

30 A preconditioned sample is cut to a size of 11 inches by 11 inches. The Machine Direction of the sample is marked and the sample is weighed on a torsion balance to ± 0.01 grams and recorded. This is known as the Sample Dry Weight. After weighing the sample, the dry sample rack (further described below) is placed on

- 41 -

the balance and the weight is recorded to ± 0.01 grams. This is known as the Rack Dry Weight.

The sample is placed on a rack and covered with a rack cover, further described below. The sample, contained by the rack and rack cover, is gently and completely submerged (to a depth of 2 to 3 inches) horizontally in a bath of distilled water at a temperature of 73 ± 2 °F for 30 ± 3 seconds.

After being submerged for 30 ± 3 seconds, the sample is gently raised (horizontally), the rack cover is gently removed, and the sample and rack are allowed to sit for a period of 120 ± 5 seconds in order to drain. While the sample is sitting in the horizontal position, water sitting on the rack is gently wiped off without touching the sample.

Following the drying of the rack and the completion of the horizontal sitting period, the rack and sample together are gently raised so that the Machine Direction is at an angle of 75° from horizontal and allowed to sit in this position for a period of 60 ± 5 seconds. After this sitting period is completed, the rack and sample are returned to a horizontal position and once again the rack is dried of standing water. The rack and sample are gently placed on the balance and the weight ± 0.01 grams is recorded. This is known as the Sample and Rack Wet Weight.

The absorbency measurement is made and recorded for three (3) machine direction samples and three (3) cross machine direction samples. During the cross machine direction measurement, the cross-machine direction of the sample is placed at an angle of 75° from horizontal.

An illustration of the sample rack and cover is shown in Figure 5. Both include frames 400 constructed of 16 GA Aluminum (Teflon Coated after Fabrication) with a cross-section shown in Figure 6. The outside dimensions 405, 410 of the frames 400 are about 13.75 inches by about 16.75 inches. Nylon thread 420 (0.3mm diameter) is tightly strung across the Aluminum frames 400 in a pattern shown in Figure 5. All diagonal threads go over those threads running perpendicular and/or parallel to the frames 400.

For each of the 6 tests, the following calculation is made (all units are grams):

- 42 -

Sample Wet Weight = Sample and Rack Wet Weight - Rack Dry Weight

Absorbency =
$$\frac{(\text{Sample Wet Weight} - \text{Sample Dry Weight})}{\text{Sample Dry Weight}}$$

- 5 The calculation is repeated for each of the 6 measurements and all 6 absorbency numbers are averaged together and reported as $\frac{g_{\text{Water}}}{g_{\text{Dry Structure}}}$ (grams of water / grams of sample dry weight).

(i) SHEAR VISCOSITY

- 10 The shear viscosity of the composition is measured using a rotational viscometer (Model DSR 500, manufactured by Rheometrics). A preheated sample composition is loaded into the barrel section of the rheometer, and substantially fills the barrel section (about 60 grams of sample is used). The barrel is held at a test temperature of 90°C. After the loading, air generally bubbles to the surface and does create problems for the run. For a more viscous samples, compaction prior to running the test may be used to rid the molten sample of entrapped air. The viscometer is
15 programmed to ramp the applied stress from 10 dyne/cm to 5000 dyne/cm. The strain experienced by the sample is measure by a strain gauge. The apparent viscosity of the composition can be derived therefrom. Then log (apparent shear viscosity) is plotted against log (shear rate) and the plot is fitted by the power law $\eta = K \gamma^{n-1}$, wherein K is
20 a material constant, γ is the shear rate. The reported shear viscosity of the starch composition herein is an extrapolation to a shear rate of 700 s⁻¹ using the power law relation.

(j) EXTENSIONAL VISCOSITY

- 25 The extensional viscosity is measured using a capillary rheometer (Model Rheograph 2003, manufactured by Geottfert). The measurements are conducted using an orifice die having a diameter D of 0.5 mm and a length L of 0.25 mm (i.e., L/D = 0.5). The die is attached to the lower end of a barrel, which is held at a test temperature of 90°C. A preheated sample composition is loaded into the barrel section of the rheometer, and substantially fills the barrel section. After the loading,
30 air generally bubbles to the surface and does create problems for the run. For more viscous compositions, compaction prior to running the test may be used to rid the molten sample of entrapped air. A piston is programmed to push the sample from the

- 43 -

barrel through the orifice die at a chosen rate. As the sample goes from the barrel through the orifice die, the sample experiences a pressure drop. An apparent viscosity can be obtained from the pressure drop and the flow rate of the sample through the orifice die. Corrections are often applied to the apparent viscosity following procedures generally known in the art. A shear correction factor and Cogswell equation are applied to the calculation of the extensional viscosity. The corrected extensional viscosity at 700 s^{-1} is reported.

It is known that the extensional viscosity can be measured using an orifice die and applying the correction factors, following the method described herein. More details of extensional viscosity measurements are disclosed in S. H. Spielberg et al., The Role Of End-Effects On Measurements Of Extensional Viskoisty In Filament Stretching Rheometers, Journal of Non-Newtonian Fluid Mechanics, Vol. 64, 1996, p. 229-267; Bhattacharya, et al., Uniaxial Extensional Viskoisty During Extrusion Cooking From Entrance Pressure Drop Method, Journal of Food Science, Vol. 59, No. 1, 1994, p. 221-226; both are hereby incorporated by reference. It is also known that the extensional viscosity can be measured using a hyperbolic or semi-hyperbolic die. Detailed disclosure of extensional viscosity measurements using a semi-hyperbolic die is disclosed in U.S. Patent No. 5,357,784, issued October 25, 1994 to Collier, the disclosure of which is incorporated herein by reference.

(k) MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION

The weight-average molecular weight (M_w) and molecular weight distribution (MWD) of starch are determined by Gel Permeation Chromatography (GPC) using a mixed bed column. Parts of the instrument are as follows:

Pump	Waters Model 600E
System controller	Waters Model 600E
Autosampler	Waters Model 717 Plus
Column	PL gel 20 μm Mixed A column (gel molecular weight ranges from 1,000 to 40,000,000) having a length of 600 mm and an internal diameter of 7.5 mm.

- 44 -

Detector	Waters Model 410 Differential Refractometer
GPC software	Waters Millenium® software

The column is calibrated with Dextran standards having molecular weights of 245,000; 350,000; 480,000; 805,000; and 2,285,000. These Dextran calibration standards are available from American Polymer Standards Corp., Mentor, OH. The calibration standards are prepared by dissolving the standards in the mobile phase to make a solution of about 2 mg/ml. The solution sits undisturbed overnight. Then it is gently swirled and filtered through a syringe filter (5 μ m Nylon membrane, Spartan-25, available from VWR) using a syringe (5 ml, Norm-Ject, available from VWR).

The starch sample is prepared by first making a mixture of 40wt% starch in tap water, with heat applied until the mixture gelatinizes. Then 1.55 grams of the gelatinized mixture is added to 22 grams of mobile phase to make a 3 mg/ml solution which is prepared by stirring for 5 minutes, placing the mixture in an oven at 105°C for one hour, removing the mixture from the oven, and cooling to room temperature. The solution is filtered using the syringe and syringe filter as described above.

The filtered standard or sample solution is taken up by the autosampler to flush out previous test materials in a 100 μ l injection loop and inject the present test material into the column. The column is held at 70°C. The sample eluted from the column is measured against the mobile phase background by a differential refractive index detector held at 50°C and with the sensitivity range set at 64. The mobile phase is DMSO with 0.1% w/v LiBr dissolved therein. The flow rate is set at 1.0ml/min and in the isocratic mode (i.e., the mobile phase is constant during the run). Each standard or sample is run through the GPC three times and the results are averaged.

The average molecular weight of the high polymer is provided by the material suppliers.

(I) THERMAL PROPERTIES

Thermal properties of the present starch compositions are determined using a TA Instruments DSC-2910 which has been calibrated with an indium metal

- 45 -

standard, which has an melting temperature (onset) of 156.6°C and a heat of melting of 6.80 calories per gram, as reported in the chemical literature. Standard DSC operating procedure per manufacturer's Operating Manual is used. Due to the volatile evolution (e.g., water vapor) from the starch composition during a DSC measurement, a high
5 volume pan equipped with an o-ring seal is used to prevent the escape of volatiles from the sample pan. The sample and an inert reference (typically an empty pan) are heated at the same rate in a controlled environment. When an actual or pseudo phase change occurs in the sample, the DSC instrument measures the heat flow to or from the sample versus that of the inert reference. The instrument is interfaced with a computer
10 for controlling the test parameters (e.g., the heating/cooling rate), and for collecting, calculating and reporting the data.

The sample is weighed into a pan and enclosed with an o-ring and a cap. A typical sample size is 25-65 milligrams. The enclosed pan is placed in the instrument and the computer is programmed for the thermal measurement as follows:

1. equilibrate at 0°C;
2. hold for 2 minutes at 0°C;
3. heat at 10°C/min to 120°C;
4. hold for 2 minutes at 120°C;
5. cool at 10°C/min to 30°C;
6. equilibrate at ambient temperaure for 24 hours, the
sample pan may be removed from the DSC instrument
and placed in a controlled environment at 30°C in this
duration;
7. return sample pan to the DSC instrument and equilibrate
at 0°C;
8. hold for 2 minutes;
9. heat at 10°C/min to 120°C;
10. hold for 2 minutes at 120°C;
11. cool at 10°C/min to 30°C and equilibrate; and
12. remove the used sample.

The computer calculates and reports the thermal analysis result as

- 46 -

differential heat flow (ΔH) versus temperature or time. Typically the differential heat flow is normalized and reported on per weight basis (i.e., cal/mg). Where the sample exhibits a pseudo phase transition, such as a glass transition, a differential of the ΔH v. time/temperature plot may be employed to more easily determine a glass transition temperature.

(m) WATER SOLUBILITY

A sample composition is made by mixing the components with heat and stirring until a substantially homogeneous mixture is formed. The melt composition is cast into a thin film by spreading it over a Teflon® sheet and cooling at ambient temperature. The film is then dried completely (i.e., no water in the film/composition) in an oven at 100°C. The dried film is then equilibrated to room temperature. The equilibrated film is ground into small pellets.

To determine the % solids in the sample, 2 to 4 grams of the ground sample is placed in a pre-weighed metal pan and the total weight of pan and sample is recorded. The weighed pan and sample is placed in a 100°C oven for 2 hours., and then taken out and weighed immediately. The % solids is calculated as follows:

$$\% \text{ Solids} = \frac{(\text{dried weight of ground sample \& pan} - \text{weight of pan})}{(\text{first weight of ground sample \& pan} - \text{weight of pan})} \times 100$$

To determine the solubility of the sample composition, weigh 10 grams of ground sample in a 250mL beaker. Add deionized water to make a total weight of 100 grams. Mix the sample and water on a stir plate for 5 minutes. After stirring, pour at least 2mL of stirred sample into a centrifuge tube. Centrifuge 1 hour at 20,000g at 10°C. Take the supernatant of the centrifuged sample and read the refractive index. The % solubility of the sample is calculated as follows:

$$\% \text{ Soluble Solids} = \frac{(\text{Refractive Index \#}) \times 1000}{\% \text{ Solids}}$$

EXAMPLES

The materials used in the Examples are as follows:

Crystal Gum® is a modified starch having a weight-average molecular weight of 100,000; Nadex® is a modified starch having a weight average molecular weight of 2,000; and Instant-n Oil® is a modified starch having a weight average molecular weight of 800,000; all are available from National Starch and Chemicals

- 47 -

Corp., Bridgewater, NJ.

Superfloc® A-130 is a carboxylated polyacrylamide having a weight-average molecular weight of 12,000,000 to 14,000,000 and is available from Cytec Co., Stamford, CT.

5 Nonionic polyacrylamides PAM-a and PAM-b having a weight-average molecular weight of 15,000,000, and 5,000,000 to 6,000,000, respectively, are available from Scientific Polymer Products, Inc., Ontario, NY.

Polyethyleneimine having a weight-average molecular weight of 750,000 is available from Aldrich Chemical Co., Milwaukee, WI.

10 Parez® 631 NC is a low molecular weight glyoxylated polyacrylamide, and Parez® 802 is a low molecular weight glyoxylated urea resin, both are available from Cytec Co., Stamford, CT.

Pluronic® F87 is nonionic poloxomer, available from BASF corp., Parsippany, NJ.

15 Urea, sucrose and glyoxal (in 40% solution in water) are available from Aldrich Chemical Co., Milwaukee, WI.

EXAMPLE 6

A melt processable composition of the invention is prepared by mixing 45wt% starch (Crystal Gum), 40.5wt% urea, 4.5 wt% sucrose, and 9.8wt% free water, and manually stirring to form a slurry. Polyacrylamide (PAM-a, Mw = 15,000,000) is dissolved in water to form a PAM aqueous solution. An aliquot of the polymer/water solution is added to the slurry. Water in the slurry is then evaporated until the weight percent of polyacrylamide in the final mixture is 0.2wt%.

20 The composition has a shear viscosity of 0.65 Pa•s and an extensional viscosity of 1863.2 Pa•s, at 700s⁻¹ and 90°C.

COMPARATIVE EXAMPLE 6b

A comparative starch composition is prepared according to Example 6 except no polyacrylamide is added to the composition. The composition has a shear viscosity of 1.35 Pa•s and an extensional viscosity of 43.02 Pa•s, at 700s⁻¹ and 90°C. Example 6 and Comparative Example 6b demonstrate that addition of a small amount of high polymer decreases the shear viscosity slightly and significantly increases the

- 48 -

extensional viscosity.

EXAMPLE 7

A melt processable composition of the invention is prepared by mixing 50wt% starch (Crystal Gum), 30wt% urea, 1.5 wt% sucrose, and 18.5wt% free water, and manually stirring to form a slurry. Polyacrylamide (Superfloc A-130, Mw = 12-14,000,000) is dissolved in water to form a PAM aqueous solution. An aliquot of the polymer/water solution is added to the slurry. Water in the slurry is then evaporated until the weight percent of polyacrylamide in the final mixture is 0.003wt%.

The composition has a shear viscosity of 1.12 Pa•s and an extensional viscosity of 46.0 Pa•s, at 700s⁻¹ and 90°C.

COMPARATIVE EXAMPLE 7b

A comparative starch composition is prepared according to Example 7 except no polyacrylamide is added to the composition. The composition has a shear viscosity of 1.23 Pa•s and an extensional viscosity of 0.69 Pa•s, at 700s⁻¹ and 90°C. Example 7 and Comparative Example 7b demonstrate that addition of a small amount of high polymer decreases the shear viscosity slightly and significantly increases the extensional viscosity.

EXAMPLE 8

A torque rheometer having a melt blowing die is used to process the composition of Example 6. The torque rheometer is illustrated in Figure 6. The torque rheometer assembly 100 includes a drive unit 110 (Model Rheocord 90 available from Haake GmbH), a barrel 120 partitioned into four temperature zones 122, 124, 126 and 128, a feed port 121, and a melt spinning die assembly 131. Twin screw elements 160 (model TW100, from Haake GmbH) are attached to the drive unit 110 and disposed within the barrel 120. A six inch wide melt blowing die assembly 131 (available from JM Laboratories, Dawsonville, GA) is connected to the end of the barrel via a pump 160. The die assembly has a spinneret plate which has 52 holes per linear inch and a hole diameter of 0.015" (0.0381cm), surrounded by a 0.02" wide air passageway 152, from which a high velocity air stream 151 impinges the extruded filaments just below the spinneret plate. The air stream has the effect of simultaneously blowing the filaments away from the spinneret and attenuating the filaments.

- 49 -

The composition of is prepared (as described in Example 6) by mixing 45wt% starch (Crystal Gum), 0.2wt % polyacrylamide (PAM-a), 40.5wt% urea, 4.5 wt% sucrose, and 9.8wt% water. The mixture is gravity-fed via feed port 121 into a torque rheometer. The torque rheometer and die assembly are set as follows:

5	Barrel Temperature	
	Zone 122	70°C
	Zone 124	90°C
	Zone 126	90°C
	Zone 128	90°C
10	Torque	100 rpm
	Die Temperature	126.7°C
	Air Temperature	126.7°C
	Air Pressure	35 psi
	Pump	40 rpm

15 The mixture is conveyed from the extruder through the pump into the melt blowing die. The resulting attenuated filaments (or fine fibers) of the invention have fiber diameters ranging from 8 to 40 microns.

Note that the weight percent starch in the melt processable composition includes the weight of starch and the weight of bound water (which is on the average about 8 wt% of the starch). It is to be understood that the as-prepared compositions are used for uniaxial and biaxial extensional processes. However, most of the water is lost during the melt process, and the resulting starch fiber, film or like product contains little or no free water. The resulting product does contain some bound water (possible by absorbing moisture from ambient environment). Therefore, the composition of the

25 resulting product may be more appropriately expressed by its solid components, calculated on a dry solid basis. For example, to calculate, on a dry solid basis, the composition of the fiber made according to Example 8, one would take out the 9.8 wt% free water from the overall composition and the 8wt% bound water from the starch, then normalize the remaining solid content to 100%. Thus, the composition of

30 the fiber of Example 8 calculated on a dry solid basis would be 47.8 wt% starch solid (without bound water), 0.23 wt% polyacrylamide, 46.8 wt% urea and 5.2 wt% sucrose.

- 50 -

EXAMPLE 9

The composition of Example 7 is melt blown into fine fibers of the invention. Figure 7a is the Scanning Electron Micrographs of fine starch fibers made from the composition of Example 7 using the process described in Example 8, shown on a 200 micron scale. Figure 7b is the Scanning Electron Micrographs of the same starch fibers shown on a 20 micron scale. Both figures show that starch fibers of Example 9 have a fairly consistent fiber diameter of about 5 microns.

EXAMPLE 10

Fifteen grams of starch (Crystal Gum, Mw=100,000) and fifteen grams of free water are mixed together at 80°C with manual stirring until the mixture becomes substantially homogeneous or gelatinizes. A high polymer (PAM-a, Mw=15,000,000) is dissolved in free water to form a PAM aqueous solution of known concentration. An aliquot of the polymer/water solution is added to the starch/water mixture such that the overall mixture contains 0.006 grams of PAM-a. Then the overall mixture is heated to evaporate water until the weight of the final mixture (starch, PAM-a and water) equals 30 grams. This mixture is subjectively shown to have suitable melt extensibility for drawing fibers.

EXAMPLES 11-13

Mixtures of starch (Crystal Gum), high polymer and water are prepared in the same manner as in Example 5. The final compositions of these mixture are shown below.

		Mw		Ex-11	Ex-12	Ex-138
Starch	Crystal Gum	100,000	wt%	49.99	49.99	46.92
Polyacrylamide	Superfloc A-130	12-14,000,000	wt%	0.02		
	PAM-b	5-6,000,000	wt%		0.02	
Polyethyleneimine		750,000	wt%			6.17
Water			wt%	49.99	49.99	46.91

These compositions of the invention are subjectively shown to have suitable melt extensibility for drawing fibers.

EXAMPLES 14-16

The following compositions are prepared in the same manner as Example 1.

- 51 -

		Mw		Ex-14	Ex-15	Ex-16
5	Starch	Crystal	wt%	41.54	20.77	20.77
	Gum	100,000				
		Nadex	wt%		20.77	
		2,000				
		Instant-n	wt%			20.77
	Oil	800,000				
	Polyacrylamide	PAM-a	wt%	0.08	0.08	0.08
		15,000,00				
		0				
	Urea		wt%	6.23	6.23	6.23
	Sucrose		wt%	6.23	6.23	6.23
10	Parez 631 NC		wt%	1.04	1.04	1.04
	Water		wt%	44.88	44.88	44.88

These compositions of the invention are expected to have suitable melt extensibility for drawing fibers. And where the water has been adjusted to about pH 2, the resulting fibers are expected to have a water solubility of less than 30%, based on the test method disclosed herein.

EXAMPLE 17

A melt processable composition is prepared by mixing 45wt% starch (Crystal Gum), 0.2wt % polyacrylamide (PAM-a), 40.5wt% urea, 4.5 wt% sucrose, and 9.8wt% water to form a slurry. The composition is melt blown into fine fibers using a torque rheometer as shown in Figure 1c in the manner described in Example 8, except the mixture is meter-fed into the torque rheometer. The torque rheometer and die assembly are set as follows:

Barrel Temperature

Zone 122 70°C

Zone 124 90°C

Zone 126 90°C

Zone 128 90°C

Torque 140 rpm

Feed Rate 16 gm/min

Die Temperature 137.8°C

- 52 -

Air Temperature	137.8°C
Air Pressure	50 psi
Pump	40 rpm

The resulting attenuated filaments (or fine fibers) of the invention have
5 fiber diameters ranging from 10 to 30 microns. The fibers are air laid onto a
papermaking forming fabric as described in U.S. Patent No. 4,637,859, with the fabrics
of U.S. Patent Nos. 5,857,498, 5,672,248, 5,211,815 and 5,098,519, all incorporated
herein by reference, also being judged suitable for this purpose.

EXAMPLE 18

10 The resultant web from the air-laying process of Example 17 is tested
for oil absorbency. A drop of a commercially available motor oil (SAE 20 grade, by
the Society of Automobile Engineers' designation) is placed on the web and on a
commercially available paper towel, respectively, for comparison of oil absorbency.
The web shows an improved oil absorbency over that of the commercial paper towel in
15 the following aspects: (1) the web absorbs oil faster than the commercial paper towel,
as shown by a shorter residence time on the surface of the web; and (2) after 30
seconds, the web has a spot size of about 1.5 to 2 times larger in diameter than that of
the commercial paper towel.

EXAMPLE 19

20 This example illustrates that the starch composition of the present
invention can be made into building materials, e.g., pressed board. A melt processable
composition is prepared by mixing 60wt% starch (Crystal Gum), 0.1wt %
polyacrylamide (SP2), 2wt% urea, 2 wt% sucrose, 1.5 wt% Parex 631 NC and 34.4
wt% water (adjusted to pH 2 with sulfuric acid) to form a slurry. The slurry is fed in to
25 a torque rheometer (Model Rheocord 90) as illustrated in Figure 1c and operated under
the conditions as described in Example 17 above, except a single capillary die (having
a 1 mm diameter and a temperature of 90°C) is used instead of a melt spinning die.
The extruded strand is dusted with saw dust or wood shavings while still wet and
sticky. The dusted strands are compressed together to form a log. The log is dried at
30 40°C in a forced air oven for two hours to get rid of the residual water from the starch
composition. The final product is a log of 47.8wt% saw dust and 52.2 wt% dried

- 53 -

starch composition.

EXAMPLE 20

This example illustrates that the present invention can be incorporated into structural materials as reinforcements. Though this example uses fibers made from a composition without high polymers. It is believed that when a composition of the present invention is used, the product would show better or equivalent performances.

A comparative cement sample is prepared as follows: 5 parts of commercially available Quikrete Anchoring cement are mixed with 1.5 part clean tap water until a thick syrup consistency is obtained. Within 5 minutes of mixing, the cement was introduced into cylindrical molds in order to obtain a constant dimension sample for evaluation. Thin wall molds 5" long and 0.23" in inner diameter (i.e., commercially available straws) are filled by driving the pasty cement mixture up from the bottom. This filling method eliminates air inclusion in the finished sample. The samples are allowed to cure for 5 days prior to evaluation. The mold is carefully scored on the outer surface so as not to damage the sample inside, then the mold is peeled away to retrieve the comparative sample (Example 20b).

A melt processable composition is prepared by mixing 45wt% starch (Durabond®, available from National Starch and Chemicals Corp., Bridgewater, NJ), 15 wt% urea, 15 wt% sorbitol, and 25 wt% water to form a slurry. The slurry is fed in to a torque rheometer (Model Rheocord 90) as illustrated in Figure 1c and operated under the condition as described in Example 19 above. The fibers are about 0.02" in diameter and are cut to 1" in length for use herein. The extruded, thin spaghetti-like strands are incorporated into cement as follows: 5 parts of commercially available Quikrete Anchoring cement are mixed with 1.5 part clean tap water and 0.5% (on a dry weight basis) starch fibers. The additional amount of water added herein is required to achieve the comparable consistency as the comparative sample above. The sample molds are filled and the samples (Example 20) are cured and retrieved in the same manner as above.

The samples are subjectively evaluated by bending to failure by hand. Example 20 are subjectively judged to be slightly weaker than the comparative Example 20b. Example 20 has an apparent density of 1.46g/linear inch while

- 54 -

comparative Example 20b has an apparent density of 1.48g/linear inch. Therefore, it is demonstrated that Example 20 offers the benefits of light weight and lower cost (on a volume basis).

EXAMPLE 21

5 This example illustrates that the composition of the present invention can prophetically be made into a controlled water release material when mixed with potting soil. The controlled water release is useful for horticultural and agricultural plants which thrive in a relatively low humidity environment and/or infrequent watering. A melt processable composition is prepared by mixing 50wt% starch
10 (Durabond®, available from National Starch and Chemicals Corp., Bridgewater, NJ), 0.1wt % polyacrylamide (SP2®), 15 wt% urea, 15 wt% sorbitol, 1.5 wt% Parex® and 18.4 wt% water to form a slurry. The slurry is fed in to a torque rheometer (Model Rheocord 90) as illustrated in Figure 1c and operated under the condition as described in Example 19 above. The extruded, thin spaghetti-like strands are allowed to dry
15 before mixing with potting soil. The ratio of starch-based strand to potting soil depends on the requirements of various types of plants. Generally, 10 wt% of starch-based strands in potting soil shows satisfactory water holding/release results.

Examples 22-24 use films made from compositions without the benefit of high polymers. It is believed that when a composition of the present invention is
20 used in each of these examples, the resultant product would show beneficial improvements in properties, e.g., lower caliper, greater flexibility.

EXAMPLE 22

This example illustrates that the compositions of the invention can be made into thin films, using a Werner & Pfleiderer ZSK-30 co-rotating twin-screw
25 extruder with a L/D ratio of 40. The screw configuration consists of four kneading sections and five conveying sections. The extruder barrel consisted of an unheated feed zone followed by seven heated zones, which are designated consecutively as Zones A, B, 1, 2, 3, 4 and 5. The barrel is controlled to the temperature profile summarized below, and the screw speed is set to 150 rpm.

30	Zone	A	B	1	2	3	4	5
	Temperature	50	50	50	95	95	95	95
	°C							

- 55 -

A melt processable composition is prepared by metering the solid materials into the extruder with a K2V-T20 volumetric feeder (available from K-Tron Inc., Pitman, NJ) and metering the liquid material into Zone 1 of the extruder with a mini pump (available from Milton-Roy, Ivyland, PA). The components are: 44wt% starch (Durabond® A, available from National Starch and Chemicals Corp., Bridgewater, NJ), 18wt% urea, 18 wt% sucrose, and 20 wt% water. The mixture is conveyed from the extruder into a Zenith B-9000 gear pump into a six-inch wide flat film die (available from Killion Extruders, Cedar Grove, NJ) at a flow rate of 33 cm³/min, wherein the gear pump is maintained at 96°C, the film die is maintained at 94°C and the die opening is set at 15 mils. The resultant film is extruded onto a 12-inch wide chill roll (available from Killion Extruders) which is maintained at 37°C. The film is then wound onto a paper core at a speed of 5 fpm. The resultant film is about 1 mil in thickness, slightly tacky to the touch, and exhibits excellent flexibility (i.e., it can be repeatedly bent at a 180 degree angle without breaking or forming a dead fold).

EXAMPLE 23

This example illustrates that the film from Example 23 can be made into a seed carrier for agricultural applications. The seed carrier film made according to this example provides an inexpensive material that can be laid down to cover and seed a large area effectively. The material holds water to facilitate the germination of the seeds, and the material is biodegradable such that no recovery and disposal are required. The film of Example 22 is placed on a single-sided release paper and sprinkled with grass seeds available from Midwestern Supply or other garden supply stores. Another sheet of single-sided release paper is placed on top of the seeds. The assembly is placed between ¼ inch (0.635cm) aluminum plates and inserted into a 6 inch by 6 inch (15.24cm by 15.24cm) Carver hot press that is preheated to 207°C. The assembly is equilibrated under low/contact pressure for one minute, then pressure is increased to a maximum pressure of 6000 pounds. The assembly is held under the maximum pressure for one minute and quickly depressurized. The assembly is taken out of the press and cooled to room temperature. The resulting film composite shows good cohesion between film and seeds such that the film composite can be handled without loss of seeds.

- 56 -

EXAMPLE 24

This example illustrates that the films of Example 22 are fusable such that the films can be made into substantially transparent bags/pouches useful as sealable food storage pouches, shopping bags, garbage bags, grocery bags, and the like. Two pieces of 4 inch by 4 inch (10.16cm by 10.16cm) films are overlaid with a piece of release paper interposed between them. The release paper should be smaller than the films so that at least three edges of the films are in direct contact with each other. A Vertrod impulse sealer (Model 24LAB-SP) is used to seal three sides of the overlaid films. The sealer is set at 50% voltage, 60 psi pressure, a six second dwell time (one second on and 5 seconds off), and for a total sealing time of one minute. The resultant bag shows uniform, welded seals on three sides. The fourth side can optional be sealed to form a completely sealed pouch.

EXAMPLE 25

This example illustrates the water-insoluble starch compositions of the present invention. A composition is prepared by mixing 50 wt% starch (Crystal Gum), a crosslinking additive (the type and the amount of the crosslinking additive are shown in the Table below) and a balance of water which has been adjusted to pH 2 using sulfuric acid. Where glyoxal (in 40% solution in water) is used, there is no need to adjust the water pH. The composition and test sample are prepared according to Test Method for Water Solubility described hereinabove. The results are shown in the Table below:

Solubility:

	<u>% Additive</u>	<u>Parez 631</u>	<u>Glyoxal</u>	<u>Parez 802</u>
	0.00%	37%	37%	37%
25	0.12%		16%	
	0.20%		10%	
	0.25%	28%		48%
	0.32%		11%	
	0.40%		7%	
30	0.50%	16%		16%
	0.75%	14%		9%
	1.00%	14%		6%
	1.50%	11%		4%

- 57 -

The disclosures of all patents, patent applications (and any patents which issue thereon, as well as any corresponding published foreign patent applications), and publications mentioned throughout this description are hereby incorporated by reference herein. It is expressly not admitted, however, that any of the documents

5 incorporated by reference herein teach or disclose the present invention.

While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is intended to cover in the appended claims all such changes and

10 modifications that are within the scope of the invention.

09914966-090601

- 58 -

CLAIMS

1. An absorbent, flexible structure comprising pseudo-thermoplastic starch fibers.
2. The structure of claim 1, wherein the starch fibers have a size ranging from about 0.01 dtex to about 135 dtex.
- 5 3. The structure of claim 1, wherein the structure has a geometric mean dry tensile strength ranging from about 10 g/cm to about 1200 g/cm, an initial geometric mean wet tensile strength ranging from about 2 g/cm to about 400 g/cm, and a geometric mean decayed wet tensile strength ranging from about 0 g/cm to about 20 g/cm.
4. The structure of claim 1, wherein the structure has a basis weight ranging from
10 10 g/m² to about 450 g/m².
5. The structure of claim 1, further comprising a plasticizer selected from the group consisting of sorbitol, monosaccharides, disaccharides, glycerol, polyvinyl alcohol, and polyethylene glycol, wherein said plasticizer comprises, based on total weight of the structure, from about 5 wt % to about 70 wt %.
- 15 6. The structure of claim 1, further comprising cross-linking agents selected from the group consisting of, polyamide-epichlorohydrin resins, urea-formaldehyde resins, glyoxylated polyacrylamide resins, melamine formaldehyde resins, polyethylenimine resins, Caldas 10 resin, CoBond 1000 resin, wherein said cross-linking agents are present in amounts ranging from about 0.1 wt % to about 10 wt. %, based on the total
20 weight of the structure.
7. The structure of claim 1, wherein the structure has an absorbency ranging from about $1 \frac{\text{g Water}}{\text{g Dry Structure}}$ to about $15 \frac{\text{g Water}}{\text{g Dry Structure}}$.
8. The structure of claim 1, wherein the structure has a total flexibility ranging from about 1.0 g/cm to about 75 g/cm.
- 25 9. A structure comprising pseudo-thermoplastic starch fibers wherein the fibers have a Tg of at least about -30 °C and the structure has a geometric mean decayed wet tensile strength ranging from about 0g/cm to about 20 g/cm and wherein said fibers have a size ranging from about 0.01 dtex to about 135 dtex.
10. An absorbent structure comprising one or more plies wherein at least one ply
30 comprises pseudo-thermoplastic starch fibers, and wherein the at least one ply has a basis weight ranging from about 10 g/m² to about 100 g/m², a GMDT ranging from

- 59 -

about 40 g/cm to about 475 g/cm, an apparent density ranging from about 0.04 g/cm³ to about 0.12 g/cm³, and an initial GMWT ranging from about 2 g/cm to about 200 g/cm.

09041966 "090604
090604" 090604

TO 3060 3354660

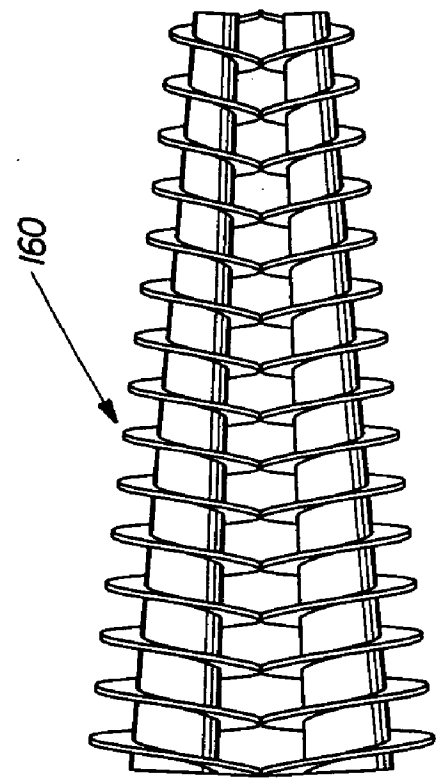
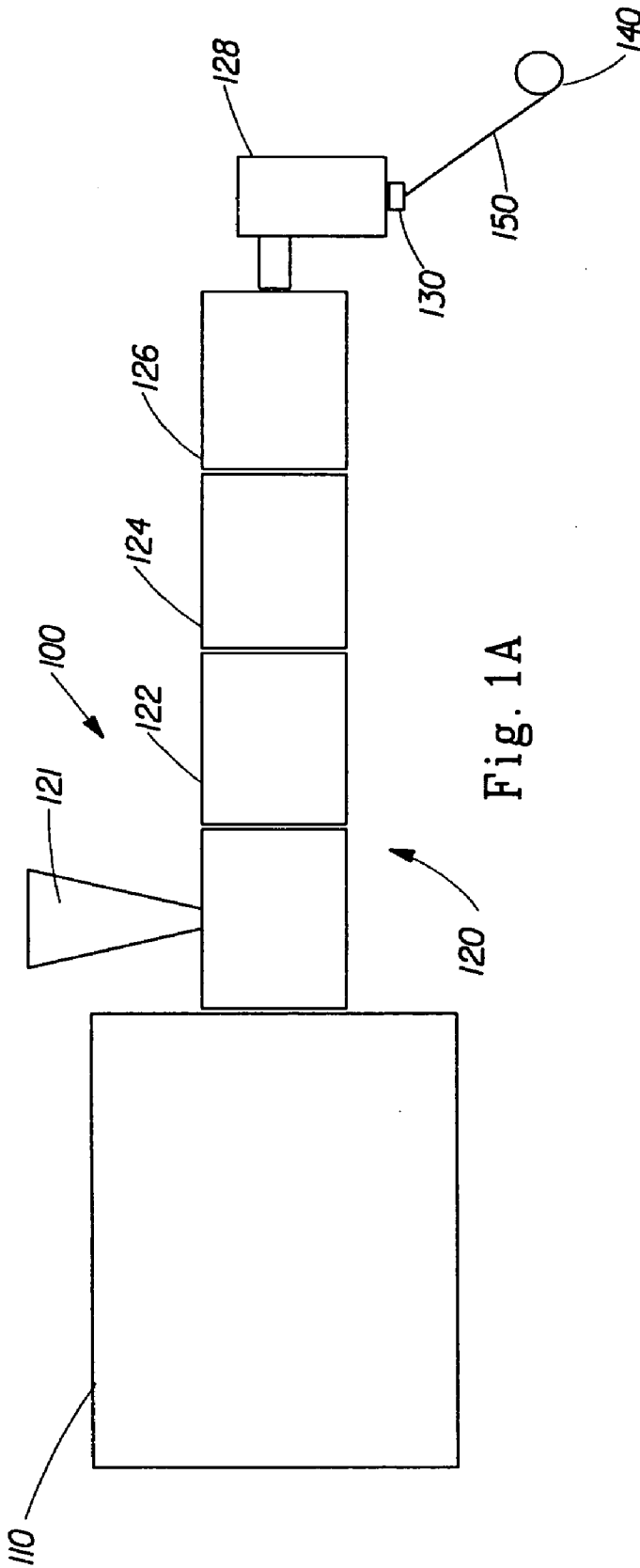


FIG. 1C

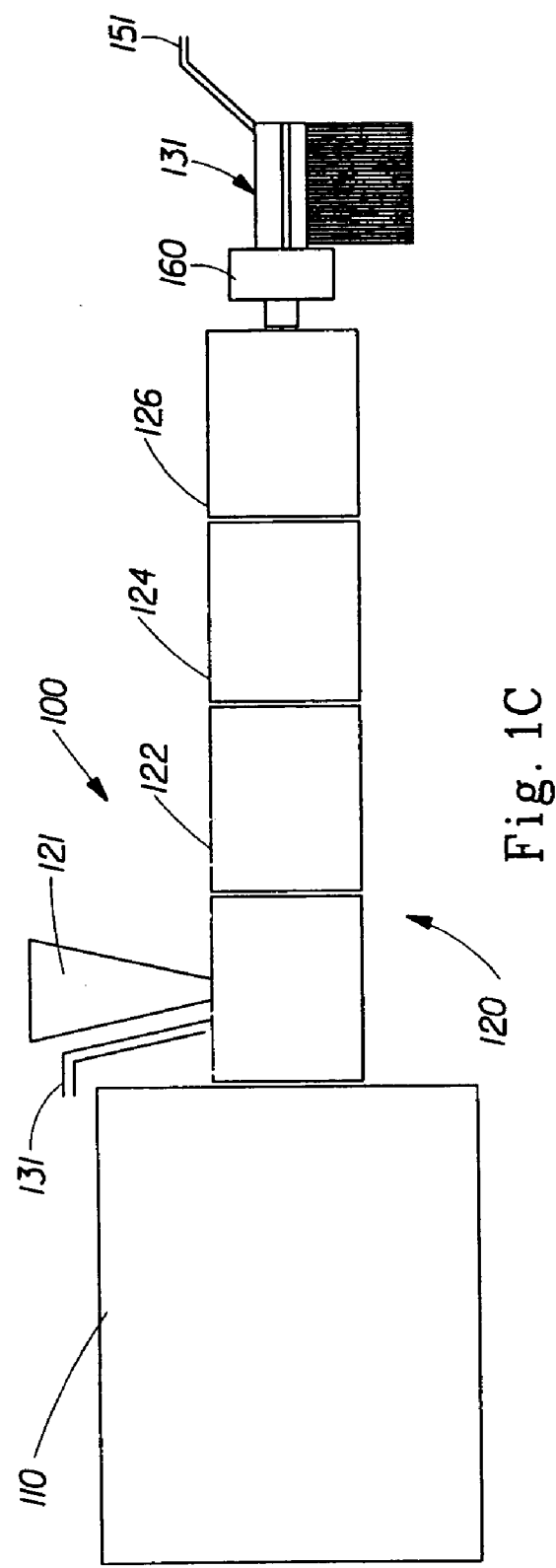


Fig. 1C

FIG. 2A

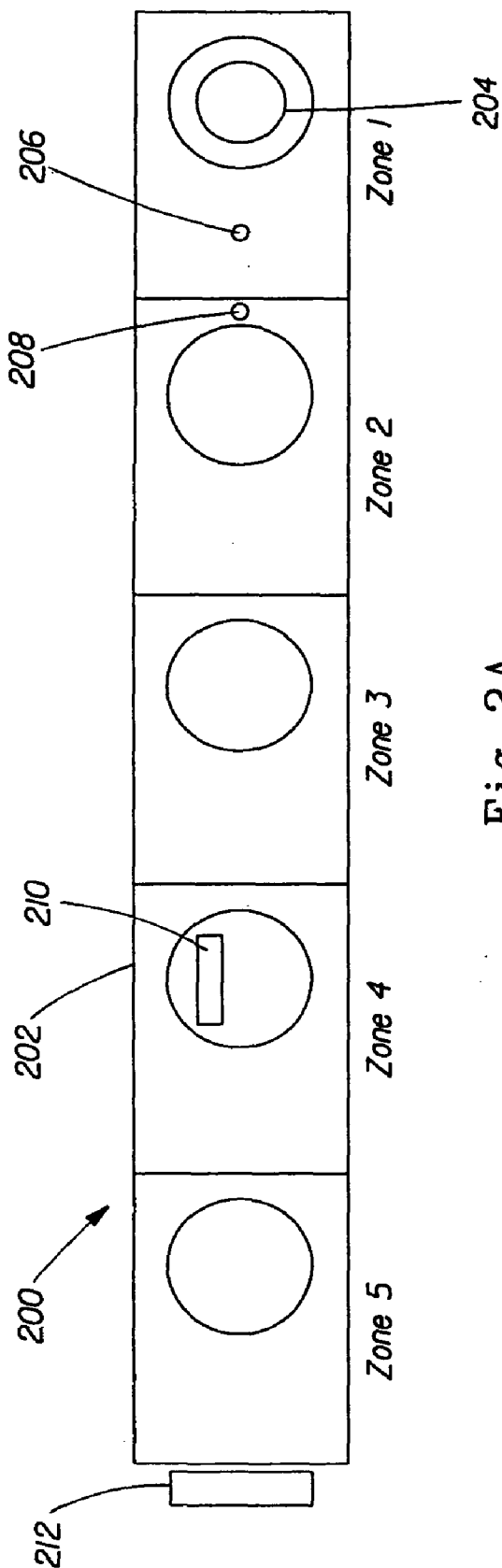


Fig. 2A

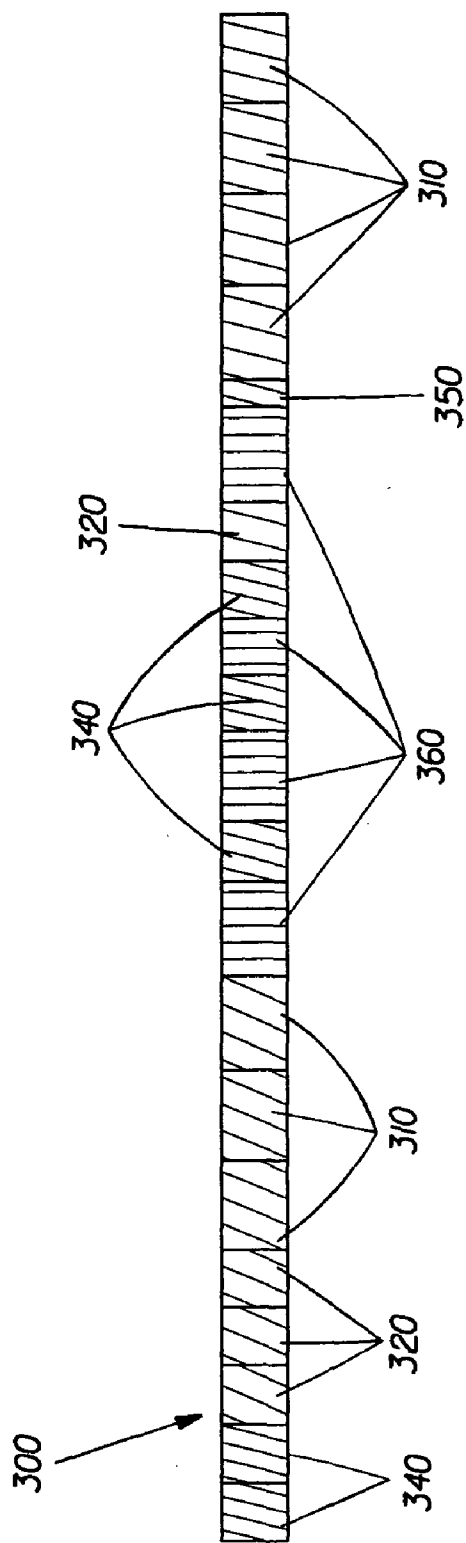


Fig. 2B

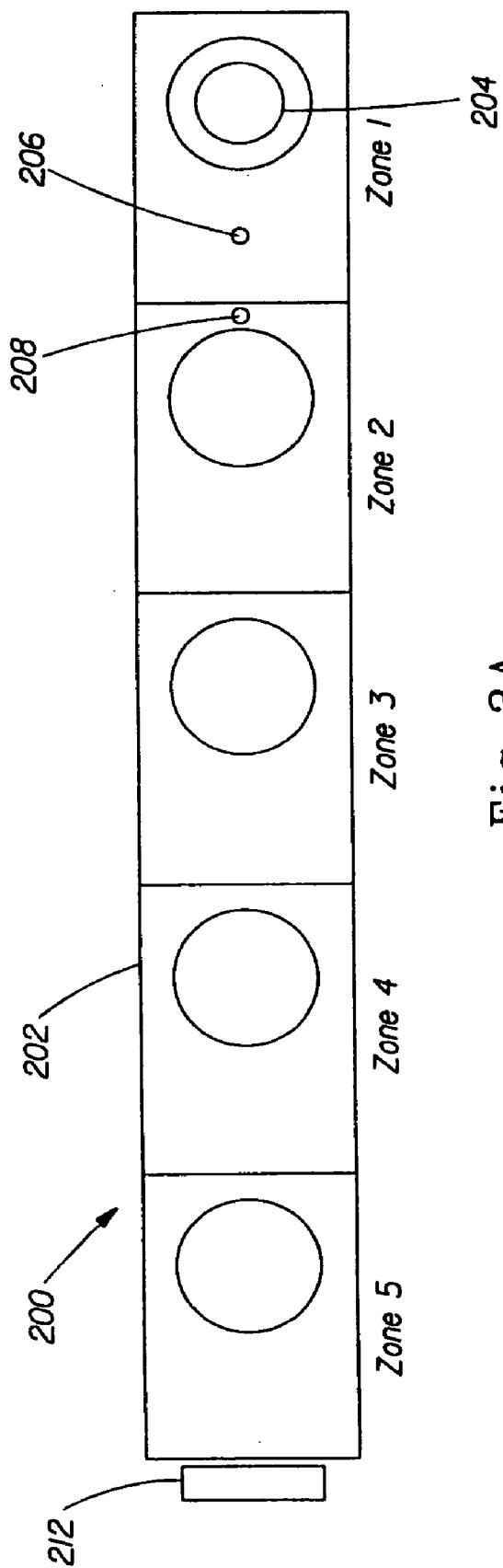


Fig. 3A

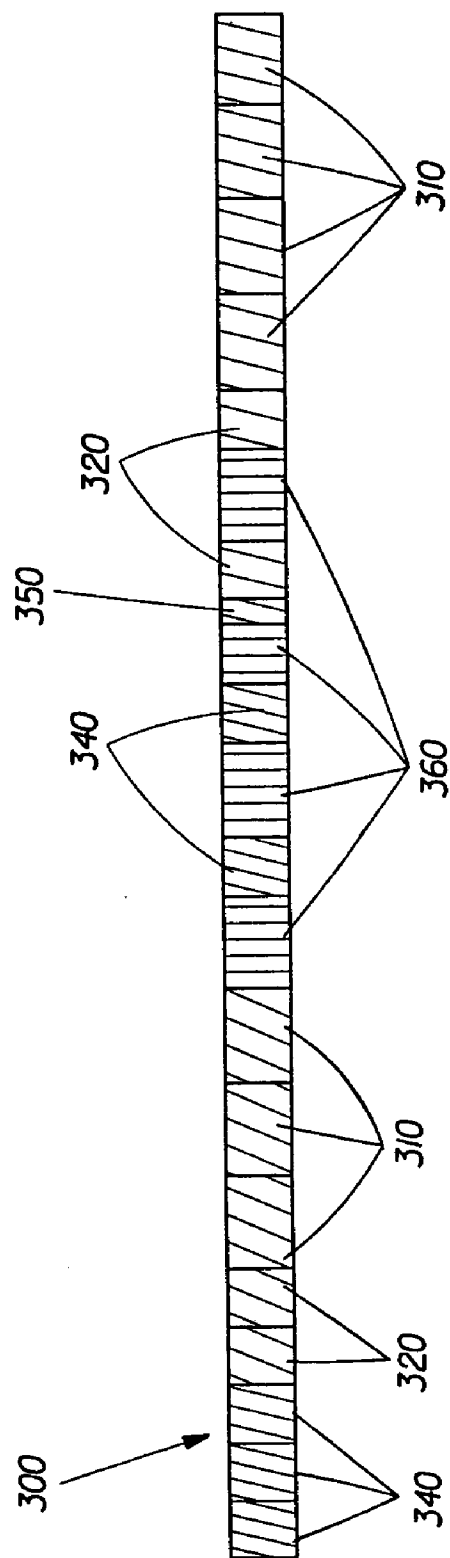


Fig. 3B

5 / 7

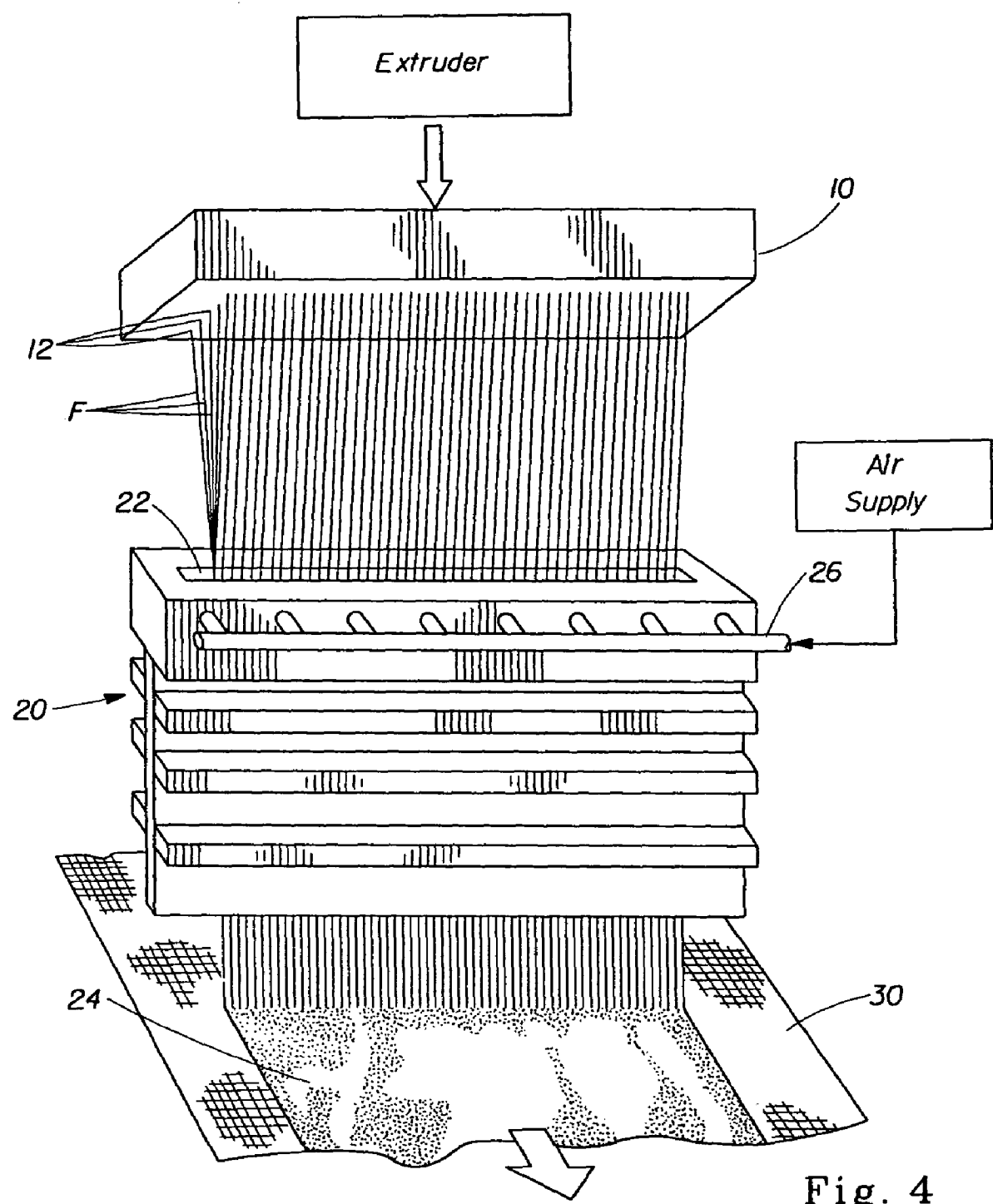


Fig. 4

6 / 7

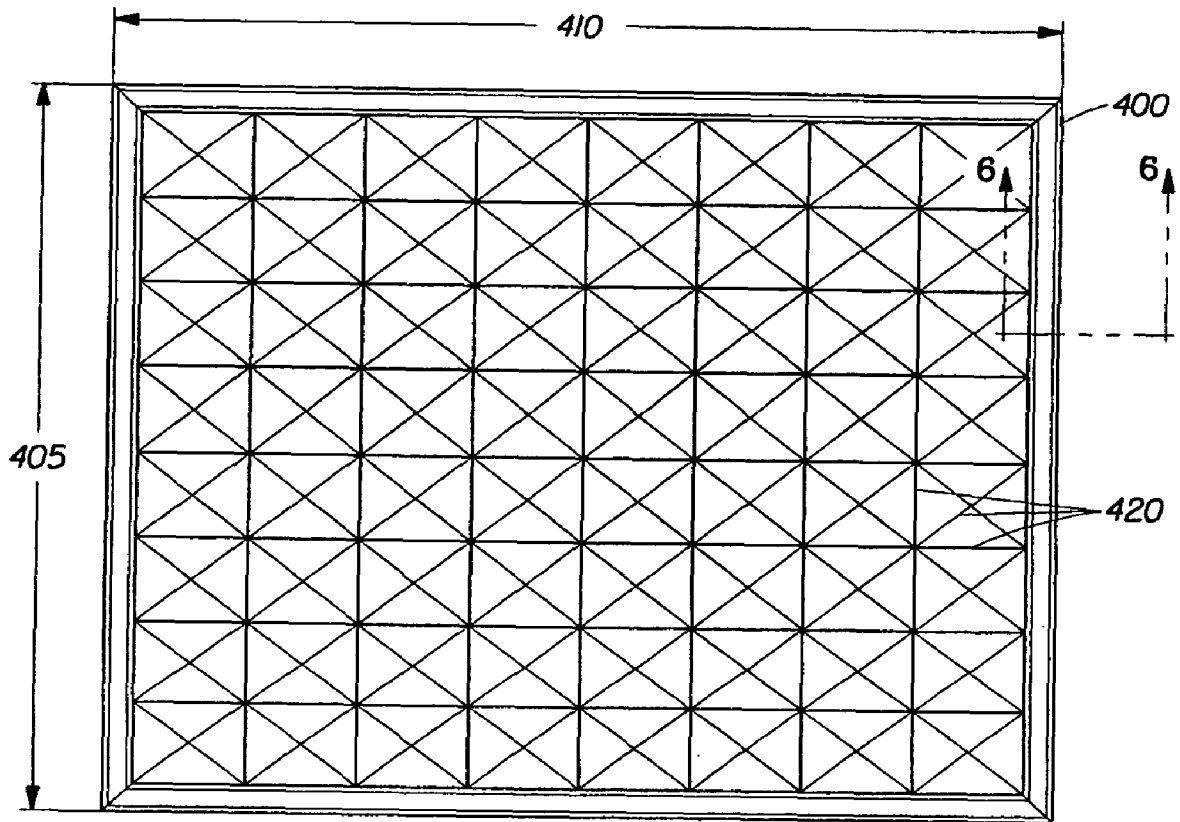


Fig. 5

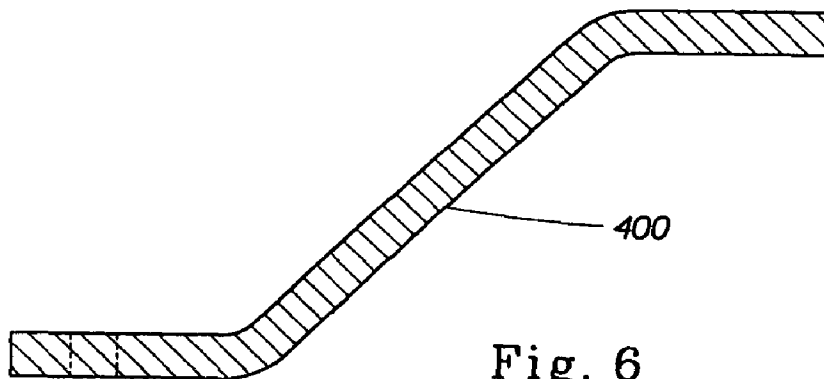



Fig. 6

7 / 7

BEST AVAILABLE COPY

sphere 20.0 μm 

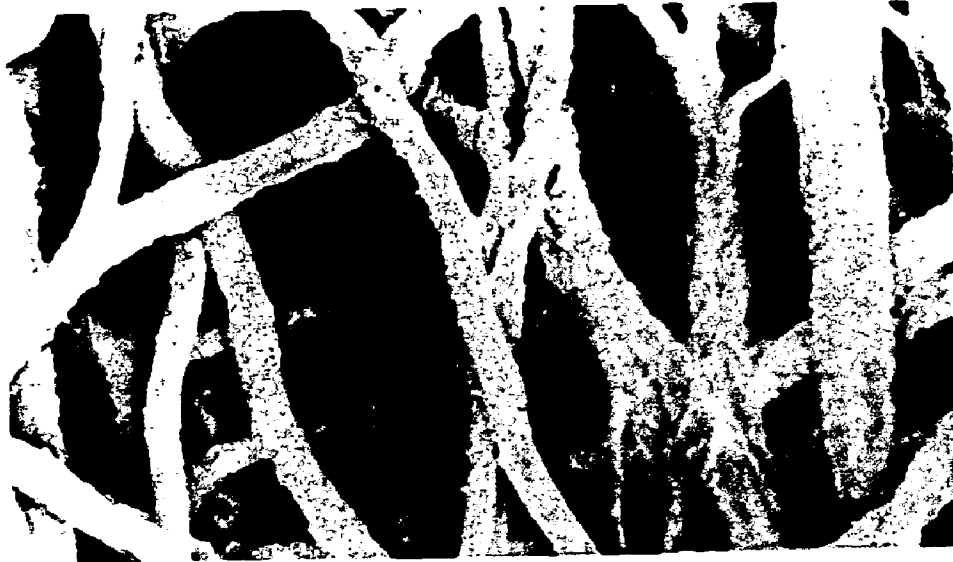



Fig. 7A

sphere 200 μm 

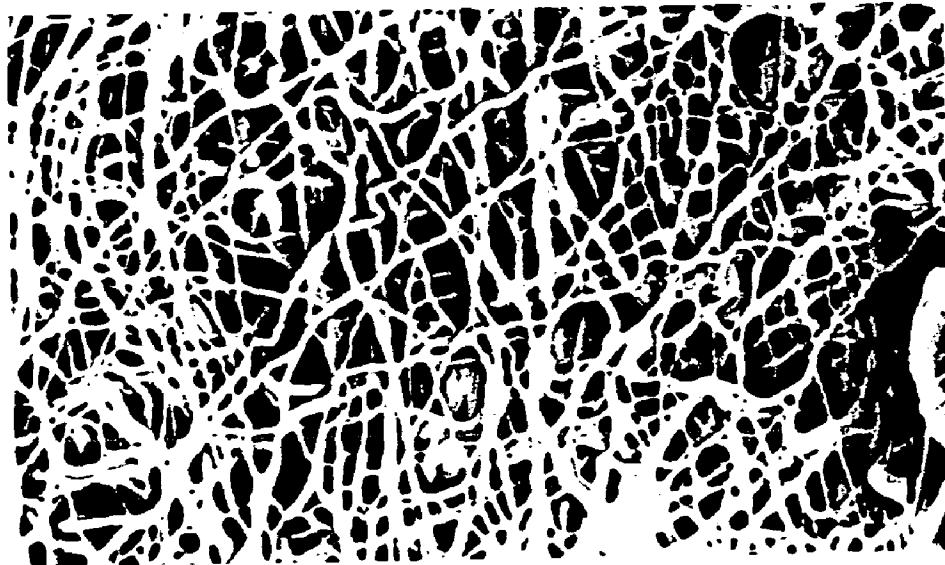


Fig. 7B

0941956.090601
109060.99617660



US005516815A

United States Patent [19]**Buehler et al.**[11] **Patent Number:** **5,516,815**[45] **Date of Patent:** **May 14, 1996**[54] **STARCH-CONTAINING FIBERS, PROCESS FOR THEIR PRODUCTION AND PRODUCTS MADE THEREFROM**[75] Inventors: **Friedrich Buehler**, Thusis; **Viktor Baron**, Domat/Ems; **Eduard Schmid**, Bonaduz; **Peter Meier**, Waedenswil; **Hans-Joachim Schultze**, Chur, all of Switzerland[73] Assignee: **EMS-Inventa AG**, Switzerland[21] Appl. No.: **390,165**[22] Filed: **Feb. 17, 1995****Related U.S. Application Data**

[62] Division of Ser. No. 973,055, Nov. 6, 1992, abandoned.

[30] **Foreign Application Priority Data**

Nov. 7, 1991 [DE] Germany 41 36 694.8

[51] **Int. Cl.⁶** **C08L 3/00**; C08L 67/02; C08L 77/02[52] **U.S. Cl.** **523/128**; 523/124; 524/47; 525/54.24[58] **Field of Search** 524/47, 50, 52, 524/54, 48; 428/364, 395; 523/124, 128; 525/54.24, 54.31[56] **References Cited****U.S. PATENT DOCUMENTS**

2,570,449	10/1951	Horsák	264/186
3,117,014	1/1964	Klug	106/213
4,366,275	12/1982	Jilano et al.	524/47
4,603,070	7/1986	Steel et al.	428/88
5,026,746	6/1991	Floyd et al.	524/50
5,095,054	3/1992	Lay et al.	524/47
5,256,711	10/1993	Tokiwa et al.	525/47
5,446,078	8/1995	Vaidya et al.	524/17

FOREIGN PATENT DOCUMENTS

327505	8/1989	European Pat. Off.
1470846	2/1969	Germany

1470965	11/1969	Germany
2001533	7/1971	Germany
2042798	5/1972	Germany
4104681	8/1991	Germany
635274	4/1950	United Kingdom
14938	12/1990	WIPO
2559	2/1992	WIPO

OTHER PUBLICATIONS

Database WPI, Week 8035, Class A, AN 80-61299C JPA-55-93,812; Jul. 17, 1980.

Database WP1, Section CH, Week 8035 JPA-55-93,812, Jul. 17, 1980.

Primary Examiner—Paul R. Michl*Assistant Examiner*—Mark L. Warzel*Attorney, Agent, or Firm*—Bierman and Muserlian[57] **ABSTRACT**

A starch fiber produced by a spinning process and comprising:

A A first amount of 1 to 100 parts of a starch melt-spinnable composition comprising

1. a second amount of 56 to 96 parts of at least one modified and/or unmodified starch,

2. a third amount of 4 to 40 parts of at least one destructuring agent,

3. a fourth amount of 0 to 4 parts of at least one additive, selected from urea, urea derivatives, emulsifiers, lubricants, and proteins and their alkali salts, components 1, 2 and 3 totaling 100 parts; and

B a fifth amount of 99 to 0 parts of at least one melt-spinnable polymer,

ingredients A and B totaling 100 parts.

In addition, there may also be included 0 to 20 parts of conventional additives for melt spinning compositions.

The invention further relates to a process for the production of these starch fibers from this melt spinning composition, and to uses for fibers which, by modification with the starch melt-spinnable composition, have special properties.

21 Claims, 1 Drawing Sheet

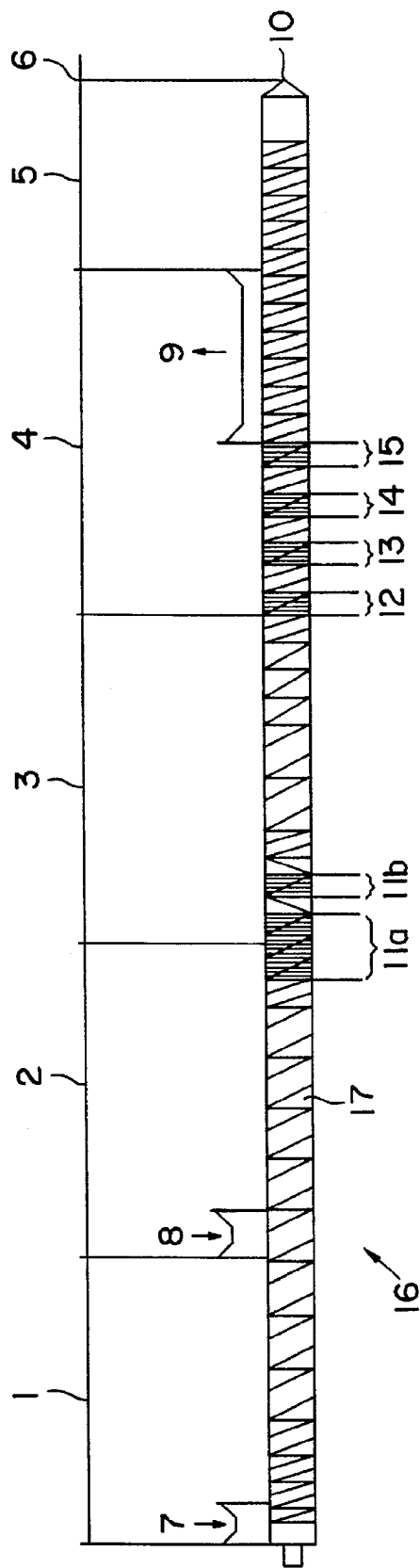


FIG. 1

STARCH-CONTAINING FIBERS, PROCESS FOR THEIR PRODUCTION AND PRODUCTS MADE THEREFROM

PRIOR APPLICATION

This application is a division of U.S. patent application Ser. No. 973,055 filed Nov. 6, 1992, now abandoned.

This application claims the priority of German Application 41 36 694.8, filed Nov. 7, 1991.

The present invention is directed to starch fibers produced from certain melt spinning compositions, their use as ingredients of other fibers, methods of producing them, and products made therefrom.

BACKGROUND OF THE INVENTION

There have been numerous attempts to make use of starch (a plant carbohydrate) as a "natural plastic" in a number of areas. It is important to commercial development that the starches be processible on standard equipment and use existing technology. However, natural starches are relatively grainy and, if they are to be suitably processed, they must first be destructured.

It has long been recognized that amylose, an important component of starch, is soluble in formaldehyde-containing aqueous solutions and alkaline aqueous solutions. In either case, the ultimate solutions obtained are relatively viscous and their stability is based primarily on the concentration of alkali or formaldehyde. Both solutions are suitable for the production of fibers, filaments, or foils.

The production of fibers, filaments, or foils from amylose has been carried out from solution in precipitation baths; i.e. wet spinning. This is set forth in, for example, DE-PS 10 63 325. However, there is no mention in this patent of any thermoplastic method.

In DE-OS 23 62 991, pharmaceutical preparations with delayed release of active ingredients for direct introduction into body cavities, are described. A mixture of the active ingredient and the polymer, including starch among other materials, is processed by melt spinning and extruded; the extrusion is then cut into pellets. These pellets are put into the usual melt spinning apparatus to produce fine fibers. The fibers are cut to a suitable length and carded dry to form "cotton" wads. The melt spinning process is mentioned very generally, but neither the process nor apparatus are not specifically described; only the use of hydroxypropyl cellulose and the extrusion are set forth. This melt spinning process is today the simplest and most widely used method for the production of synthetic filaments.

BRIEF DESCRIPTION OF THE INVENTION

It is, therefore, an object of the invention to provide novel starch or starch-modified fibers with special properties which can be produced from a biodegradable melt spinning composition, said composition to be spun by the current melt spinning processes and equipment. It is also an object of the invention to permit the use of the fibers thus produced, endowed with special properties, in a variety of applications.

It has now been found that the starch melt-spinnable compositions can be processed with polyamides, polyesters, and other polymers by thermoplastic methods to form fibers. For special applications, depending on the degree to which the starch or starch derivative is hydrophilic, portions soluble in cold water, soluble in hot water, or insoluble in water can be built into the synthetic fiber. For example, when

such fibers, containing small amounts of starch melt-spinnable compositions insoluble in hot water, are treated with hot water, porous fibers are obtained. If the fiber contains more than 50% starch molding composition, the treatment with hot water produces a fine powder precipitate of the fiber polymer, which sinks if its density is greater than that of water. The starch-laden waste water is completely biodegradable, and the polymer precipitate can be filtered and regenerated.

Surprisingly, it has been found that, in homogeneous starch melt-spinnable compositions with polyesters, polyethers, or linear aliphatic polyamides, the thermoplastic, finely-dispersed, polymer component itself is also amenable to biodegradation. The more homogeneous the polymer component is with the starch molding composition, the faster the biodegradation takes place. Further, the rate of degradation depends on the length of the carbon chain between hydrolyzable groups. If this starch molding composition is used without the polymer component, an unusually quick biodegradation in less than 20 days is observed.

The invention also relates to starch fibers which can be spun by known methods thermoplastically from a starch molding composition. This melt-spinnable composition is notable for its easy processibility and can produce fibers, which are useful for biodegradable fabrics, nonwovens, knits, etc., and can serve as modifiers of traditional fibers; in particular, for filters, household fabrics, sanitary nonwovens, and the like. Fabrics and nonwovens made of these materials are usable for bags, cloths, nets, and especially for packing agricultural products of all kinds. Additional areas of use are root packings of plants, trees, flowers, and the like.

Further, the invention relates to areas of use for fibers which are given special properties by modification with the starch melt-spinnable composition. By the addition of starch, the disadvantage of the synthetic textile fibers with respect to the low moisture absorption can be eliminated and wearing comfort comparable to cotton fabrics achieved. Moreover, the high density of the starch melt-spinnable compositions provides higher weights and offers particular advantages where heavy fibers are required.

Especially advantageous is the use of fast biodegradable fibers as cigarette filters. Further, biodegradable fibers are also desirable for sanitary nonwovens, fabrics, operating room textiles, diapers, absorbent "cotton" and wound dressing materials.

In conjunction with starch, the properties of resorbable materials such as polyhydrobutyric acid, polyhydrovaleric acid, polylactides, polyglycolides, as well as their copolymers and blends, can be modified and processed to provide resorbable filaments and fabrics.

In the case of bi- or multi-component fibers containing starch melt-spinnable compositions, due to the hydrophilic nature of selectable starches, the starch melt-spinnable compositions, which are stable to cold water in the cooling bath, can be dissolved out in hot water, thereby obtaining porous fibers. This method can be used also for the production of hollow fibers, through the formation of a coextruded starch core. The fibers of the present invention can, of course, be produced in all shapes; e.g. round, star-shaped, and angular. The cores may be incorporated continuously or intermittently, and can subsequently be dissolved out wholly or partially.

The starch melt-spinnable composition can be used as matrix material in production of superfine fibers. After spinning the superfine fibers in the matrix, the matrix can be dissolved away with hot water in an ecologically friendly

and economical manner and can either be reused or disposed of by biodegradation. These fibers can be used, for example, for the production of imitation suede or extremely fine-pored filter nonwoven materials.

The inventive melt-spinnable composition is also capable of giving synthetic fibers an antistatic finish. In addition, if the starch melt-spinnable composition contains residual water, it is suitable for flameproof finishing and reduces drip problems in synthetic fibers in a manner similar to metal hydroxide finishes in plastics.

Starch-modified fibers can serve for the production of separating yarns destroyable with hot water. They are useful as temporary or permanent adhesive fibers, depending on their water solubility, allowing temporary bondings, e.g. in nonwovens, to be separated again by steam treatment. Thus recyclable composite nonwovens of different materials can be produced.

For the production of permanent bondings, these fibers can be finished with reactive systems such as isocyanates; hindered isocyanates; formaldehydes; epoxides; hindered epoxides; anhydrides; and ester-, amide-, and carbamate-forming materials; and crosslinked immediately or subsequently.

Starch-modified fibers can be used in composite fiber technology as hot-water soluble fabric layers in order to keep different fiber materials separated. Later, after separation by hot water treatment, recycling of the pure material is possible.

Nowadays, synthetic fibers are used for paper reinforcement and for wet fiber finishing. However, they have the disadvantage that, when the paper is disposed of, these fibers are non-biodegradable. With the aid of starch-modified fibers, reinforced papers can be produced which are fully biodegradable. Papers with high starch fiber content are especially suitable as release papers, and insulating materials, as well as papers having improved sliding properties and printability, which are particularly suitable for use in photocopiers. On recycling, starch-modified paper reinforcement fibers break down into the water-soluble starch component, which remains in the pulp, and a pulverized polymer component which sinks, not being water-soluble and having a density higher than water, and which can thus be separated from the pulp for reutilization.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic view of a twin-screw extruder useful in the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The starch fibers according to the invention are made from a melt spinning composition comprising the following components. Throughout the specification and claims, all parts and percentages are by weight:

- A. 1 to 100 parts of a starch melt-spinnable composition comprising
 1. 56 to 96 parts of at least one modified and/or unmodified starch,
 2. 4 to 10 parts of at least one destructuring agent,
 3. 0 to 4 parts of at least one additive, selected from the group consisting of urea, urea derivatives, emulsifiers, lubricants, proteins and their alkali salts, and mixtures thereof,
- the parts of components 1, 2, and 3 totaling 100; and

B. 99 to 0 parts of at least one melt-spinnable polymer, the parts by weight of components (A) and (B) adding up to 100.

In addition to the foregoing there may also be present 0 to 20 parts of materials of the prior art customarily added to melt spinning compositions.

Preferably, the additive consists of at least one of 0.1 to 2 parts of urea and/or urea derivatives, and 0.1 to 2 parts of at least one emulsifier. Preferably, the melt spinning composition consists of 20 to 95 parts, especially 20 to 80 parts, and most particularly 50 to 60 parts, of component A and of 80 to 5, preferably 80 to 20, more particularly 50 to 20, parts of component B. Component A advantageously contains the destructuring agent in quantities of 9 to 40 parts, more desirably 10 to 30 parts.

In a preferred embodiment, the starch fiber according to the invention is produced by a melt spinning process and which consists of the following components:

A. 10 to 100, preferably 30 to 100, parts of a starch melt-spinnable composition comprising

1. 66 to 90 parts of at least one modified and/or unmodified starch,
2. 10 to 30 parts of at least one destructuring agent,
3. 0 to 4 parts of at least one additive selected from the group consisting of urea, urea derivatives, emulsifiers, and lubricants,

the parts of components 1, 2, and 3 adding up to 100; and

B. 90 to 0 parts, preferably 70 to 0 parts, of at least one melt-spinnable polymer,

the parts of components A and B adding up to 100.

In addition, there may also be present 0 to 10 parts of materials of the prior art customarily added to melt spinning compositions.

A particularly preferred form of the melt spinning composition according to the invention contains component A in an amount of from 20 to 95, more particularly 20 to 80, parts and component B in an amount of from 80 to 5, more particularly 80 to 20, parts, 50 to 80 parts of component A and 50 to 20 parts of component B being most preferred.

The chemically modified or unmodified starch to be used according to the invention advantageously has a natural water content of 5% to 16%, preferably 5% to 12%, more particularly 6% to 8% by weight. The preferred starch melt-spinnable composition can be produced by the process described in U.S. patent application Ser. No. 890,563, filed May 28, 1991, now U.S. Pat. No. 5,316,578. The starch having a natural water content, in the presence of at least one plasticizer, urea or urea derivative, and at least one emulsifier, is broken down at suitable elevated temperatures and pressures in an extruder and extruded as a melt.

In the present process, this starch is then chemically modified by reaction of its OH groups with alkylene oxides or other ether-, ester-, urethane-, carbamate- and/or isocyanate-forming substances. Preferred are hydroxy-, C₂- to C₆ alkyl-, acetyl- or carbamate-starches or mixtures thereof.

The degree of substitution of the chemically modified starch is 0.01 to 3.0, preferably 0.05 to 1.0. The amylose content of the modified or unmodified starch used is 20% to 100%, preferably 50% to 100%, and most preferably 65% to 100%. For water-resistant starch fibers, hydrophobic starch derivatives of a degree of substitution of 2 to 3 are particularly useful.

The plasticizer is advantageously an organic compound having at least one hydroxyl group, preferably a polyol. Sorbitol, mannitol, D-glucose, ethylene glycol, polyethylene glycol, propylene glycol, and mixtures thereof have been found to be especially suitable.

The additive is present in quantities of from 0 to 4 parts. Preferred are urea, urea derivatives, emulsifiers, lubricants, proteins and their alkali salts, and mixtures thereof. The urea and/or urea derivatives are employed in amounts of 0.1 to 2 parts, more preferably 0.1 to 1 parts, and most preferably 1 part.

In a preferred embodiment, component A consists of 70 parts hydroxyethyl and/or hydroxypropyl starch with a degree of substitution of 0.06 and an amylose content of 50%, 15 parts glycerol, 13.8 parts sorbitol, 1 part urea, and 0.2 parts magnesium stearate. As component B, suitable thermoplastic polymers having a melting or softening point of 50° to 220° C. are recommended.

As component B, aliphatic polyamides and polyesters having a melting or softening point of 50° to 160° C. and a melt-flow index (MFI) of 50 to 8000 Pa.s (at 160° C. and 21.2N.) are particularly recommended. Most advantageous are homo- and/or copolyamides from omega-amino carboxylic acids and lactams, as well as homo- and/or copolyamides derived from diamines (including polyether diamines), dicarboxylic acids, and/or dimerized fatty acids. Amongst the diamines, aliphatic diamines are most advisable and, amongst the dicarboxylic acids, those which are linear are worthy of special mention.

As to the chain length, the omega-amino carboxylic acids advantageously have 2 to 12 carbon atoms, preferably 6 to 12 carbon atoms. The lactams have desirably 4 to 12 carbon atoms, most desirably 6 to 12 carbon atoms. The more useful diamines have 2 to 12 carbon atoms, preferably 2 to 6 carbon atoms. The dicarboxylic acids of particular note have 2 to 12 carbon atoms and are linear.

Examples of specific compounds are lactam-6, lactam-11, lactam-12, omega-amino caproic acid, omega-amino undecanoic acid, omega amino dodecanoic acid, dimethylene diamine, tetramethylene diamine, hexamethylene diamine, polyether diamine, oxalic acid, succinic acid, adipic acid, sebacic acid, dodecane diacid, azelaic acid, dimerized fatty acid from saturated fatty acids with 17 to 19 atoms, and mixtures thereof.

With respect to biodegradability, materials are preferred which are themselves biodegradable, such as polycaprolactone, polyhydroxybutyrate, polyhydroxyvalerate, polylactides, and mixtures thereof. Also useful are linear aliphatic polymers, such as polyamides, polyesters, polyethers, polyurethanes, which are biodegraded in homogeneous starch-polymer mixtures.

As additional materials, one or more of optic brighteners, stabilizers, antioxidants, flame retardants, dyes, pigments, fillers, processing adjuvants, plasticizers, crosslinking or branching agents, etc. can be used in amounts totaling from 0 to 20 parts.

The process of the invention for the production of starch fibers from a melt spinning composition as discussed above comprises

- (a) production of a spinning melt having a water content of 1 to 15% by weight based on said melt-spinnable composition by fusing said melt-spinnable composition and said melt-spinnable polymer in a ratio of 1:99 to 100:0 by weight to form said melt whereby components A and B have been granulated separately or jointly before
- (b) transporting said melt without substantial cooling to a spinner packet whereby a melt filtration is alternately suspended
- (c) melt spinning said melt to form said fiber
- (d) cooling said fiber
- (e) applying a spinning preparation

(f) drawing and winding the said fiber

(g) aftertreatment of the cooled fiber

In step (a), component A, component B, if present, and the optional prior art materials, are fused together in a compounding extruder in a ratio of component A to B of, for example, 1:99 to 100:0 parts. Without cooling, the starch melt-spinnable composition so produced is conveyed to the spinnerette packet. It can be further processed by melt spinning into fibers whereby, in a preferred manner, a granulate is first produced, which is then employed for the production of the spinning melt and fibers.

The water content of the spinning granulate is desirably adjusted to 1% to 15% by weight, preferably to 2% to 10% by weight, more particularly to 5% to 8% by weight, based on the starch melt-spinnable composition.

Production of the fibers according to the invention from the melt spinning compositions occurs by the usual melt spinning process. Monofilaments, multifilaments, staple fibers, nonwovens, hollow fibers, multi-component fibers, and superfine fibers embedded in a matrix, can all be produced by using the compositions and methods of the present invention. The process for the production of these fibers may be in one stage, with a compounding extruder producing the molding composition e.g. by the process described in German Patent Application P 41 17 628.6, and conveying it without cooling through a melt filter to the spinnerette packet. Alternatively, two stages, starting with a previously produced granulate which is melted in a conveyor extruder and conveyed to the spinnerette packet, may also be used.

The spinnerette packet consists of a known assembly, the funnel-shaped distributor insert being adapted to the fluidity of the melt, so that every nozzle opening has the same rate of flow. The spinnerette plate may have one to several thousand nozzle bores with hole diameters customary for fiber production.

After the spinnerette packet, the filaments pass through a cooling section, are provided with a spinning preparation, and are wound on spools or deposited in cans. As cooling media, liquids or gases are used. Suitable liquids for water-soluble fibers are nonpolar, incompatible with water, and with low solidification points. For water-resistant fibers, water is used. As dry cooling sections, quenching chambers in which the filaments are cooled with cold air, nitrogen, or carbon dioxide as cooling gas, are used. The wound or deposited filaments can now be guided over a drawing unit, drawn, and wound as smooth filaments or, if desired, crimped, fixed, and cut to form staple fibers. Alternatively, the filaments can be further drawn directly and wound as smooth filament.

Suitable drawing units are, for smooth multifilaments, draw-twisting, draw-winding machines, and spin-draw-winding units; for monofilaments, compact monofil spinning-drawing units; and for staple fibers, drawing lines and compact spinning-drawing lines. These drawing lines are equipped with heatable or partly unheated drawing units with rollers as well as idler rollers. They may also have steam, hot air, and infrared ducts, as well as brightening devices, crimping units, dryers, cutters, and other units.

Following the drawing process, all known finishing measures can be carried out. For example, a brightener, which preferably contains emulsifiers, may be applied. The emulsifiers become anchored to the polar head group at the surface, thereby locating the nonpolar end on the outside. The fixing or relaxing of the filaments or fibers is usually carried out on these installations after the stretching operation. To produce especially fine counts, threads of pure

starch, and polymers with a high starch content, can be subjected to plastic elongation, these threads being treated in the elongation step preferably with steam and then dried with air. The rapidly spun multifilaments can be draw-textured on machines known for this purpose in the usual manner.

For the production of multi-component fibers or superfine fibers embedded in a matrix, the starch melt and the polymer melt are conveyed to the spinnerettes separately and combined without phase mixing. In a preferred process, the fibers are conducted into a heated bath, which preferably contains water, the water-soluble starch component being dissolved out of the fiber either completely or sectionwise.

In a special form of the invention, fibers with defined profiles or superfine fibers are obtained which are suitable, for example, for the production of imitation suede. In a further embodiment, the fiber is conducted into the solvent bath or heated waterbath, the soluble sheath or core being dissolved thereby. In this manner, hollow fibers with defined cavities (round, star-shaped, angular, etc.) and adjustable cut lengths can be obtained.

In particular, the present invention lends itself to the production of

- a) starch fibers without polymer additions
 - b) synthetic fibers with starch addition
 - c) porous synthetic fibers
 - d) synthetic hollow fibers or starch hollow fibers
 - e) synthetic superfine fibers or starch superfine fibers
 - f) starch fibers containing polyhydroxybutyric acid, polyhydroxyvaleric acid, polycaprolactone, polylactides, and/or polyglycolides
 - g) starch derivative fibers without polymer additions
 - h) starch derivative fibers with polymer additions
- Some of the advantages of the above fibers are
- a) Fast biodegradability
 - b) elevated density, antistatic properties, water solubility, and wet strength
 - c) thermal insulation action of hollow fibers
 - d) absorbance in porous and hollow fibers
 - e) low density in porous fibers
 - f) release properties
 - h) moisture transmission

With the invention it has thus been possible, for the first time, to find a favorable and ecologically friendly composition by which the moisture content of synthetic fibers can be controlled, and which is compatible with traditional fiber materials. For subsequent uses, this hydrophilic additive can be removed after the production of the fiber, ideally through simple, ecologically friendly processes. The wash solution obtained is completely biodegradable, causing no pollution of any kind. On washing out the hot-water-soluble adjuvant, porous fibers or fibers with defined cavities are formed. In another application, the plastic material decomposes in powder form after dissolution of the hydrophilic component. Due to their starch content, fibers according to the invention are antistatic and flame-retardant. In special applications, such as in carpets, their higher densities are of advantage.

Preferred applications for starch fibers without polymer additions, i.e. without component B, and for synthetic fibers with starch addition, are in the sector of paper conversion and paper reinforcement. Where complete biodegradability of all components is demanded, or polymer additions are to be separated by a process described above and reused after pulverization, the inventive materials are useful. Especially preferred is the production of biodegradable filters, in particular cigarette filters or sanitary nonwovens, and the production of biodegradable textile fabrics for one-time use.

Preferred also is the production of air, oil, and vacuum cleaner filters. Starch-modified, washable synthetic fibers are most useful as textile fabrics for improved moisture absorption, to increase the wearing comfort of clothing.

Starch or starch-modified synthetic fibers destroyable with steam or hot water are suitable for the production of composite nonwovens, composite fabrics, or knit goods consisting of different materials which, after the destruction of the binding fibers, are to be reused without further processing. These low-pollution fibers are useful in particular for the manufacture of fiber composite materials where removable construction aids are needed, or where removable separating fabrics, as between individual fiber plies, is advantageous. Especially preferred are bonding fibers which increase the strength of temporary bonds and can be removed after they have carried out their intended function. A special advantage of these hot-water-destroyable fibers is that nearly all synthetic fibers are insoluble in water so that their form is preserved after the destruction of the binding fibers; the starch component can be dissolved and is biodegradable, and the plastic component of the binding fiber decomposes to powder and can be reused.

Porous fibers or hollow fibers can be used as especially light-weight insulating materials. Because of their rough surfaces, the porous fibers are especially suitable for needling to nonwovens and fabrics. Furthermore, these fibers, having considerably increased surface area, are usable for the manufacture of absorbent nonwovens, in particular for diapers, "cotton" oakum, or for other filter materials of high absorption.

Starch fibers which are modified with polymers resorbable by the human body, such as polyhydroxybutyric acid (PHB), polyhydroxyvaleric acid (PHV), polylactides, and polyglycolides, can be used as surgical sutures. Superfine synthetic fibers, made with the aid of a starch matrix, are suitable for the manufacture of superfine fabrics which can be employed as imitation suede or as filter materials. The fibers according to the invention may have round, hollow, and multilobal fiber cross-sections.

For the aftertreatment of the fibers the following possibilities exist:

- a) Physical aftertreatment, such as crimping; and
- b) chemical aftertreatment; i.e. all chemical aftertreatment and conversion methods such as those used in paper conversion as well as in cellulose treatment.

For the production of foam fibers, an alternative treatment option may consist in the addition of foaming agents to the melt spinning composition. Substances which develop gases under the treatment conditions may also be used for this purpose.

In the accompanying drawing, constituting a part hereof and in which like reference characters indicate like parts, FIG. 1 is a schematic view of a twin-screw extruder useful in the present invention.

Extruder 16 is equipped with corotational twin screws 17 which extend through independently heat controlled zones 1 to 6. Feed opening 7, which may be equipped with two proportioning devices (not shown) for solids permits charging the material to be processed.

Second feed opening 8 comprises a proportioning device for liquids. The solids and the liquids are introduced in the appropriate ratios through feed openings 7 and 8, respectively. Shafts 17 rotate and transfer the material being processed through zones 1 to 6, extruding the material through nozzle 10.

It is important to provide two-stage kneading chamber 11a and 11b; additional optional kneading chambers 12 to 15 may also be present. The latter would be used for the incorporation of further materials as is known in the art.

The following examples are to illustrate the invention, but are not limiting.

I. Production of the starch molding composition (component A)

EXAMPLE 1

The starch melt-spinnable composition, which was subsequently granulated, comprises 70 parts hydroxypropyl corn starch having a degree of substitution of 0.06 and an amylose content of 50% 15 parts glycerol, 12.8 parts sorbitol, 2 parts urea, and 0.2 parts magnesium stearate.

The extruder is set as follows:

a) Heating zones:	1 room temperature 2 130° C. 3 130° C. 4 100° C. 5 100° C. 6 150° C.
b) Pressure Zone 6:	$3 \times 10^5 - 4 \times 10^5$ Pa (30–40 bar)
c) Torque:	70%
d) Vacuum:	-4×10^4 Pa (–0.4 bar)

The corotational, closely meshing twin screw extruder with a screw as shown in FIG. 1 has a screw length to diameter ratio of 41. 70 parts of hydroxypropyl corn starch (having a degree of substitution of 0.06 and an amylose content of 50%) and 12.8% of sorbitol are separately introduced at feed opening 7 in zone 1 of extruder 16. Rotating shafts 17 convey the mixture to zone 2, where a prehomogenized mixture of 0.2 parts of magnesium stearate and 2.0 parts of urea (both dissolved in 15 parts of glycerol) at 60° C. are introduced at feed opening 8. The ingredients are conveyed through kneading chamber 11a and 11b between zones 2 and 3 where mixing and destructureization of the starch takes place, resulting in the formation of a homogeneous melt.

Thereafter, in zone 4, a vacuum is applied at point 9 to degasify the melt. The melt is then carried through heating zone 5 to zone 6 where it is extruded through nozzle 10. Nozzle 10 is an expansion nozzle wherein the diameter of the opening is 3.0 mm and the extrusion diameter is 4.0 mm. The extrusion is cooled and, if desired, granulated.

The yellowish granulate has a water content of 5% to 8% as compared to a water content of the starch of 9% to 12%. The homogeneous, thermoplastically processible starch melt thus produced has a melt viscosity of 3000 Pa.s at 160° C. and 236.4N.

II. Preparation of the starch-plastic melt-spinnable compositions for fiber production

EXAMPLES 2 to 32

The starch granulate of Example 1 is mixed with the granulate of synthetic fiber material (component B) and introduced into zone 1 of twin-screw extruder 16 (ZSK-30

from Werner & Pfleiderer) with 6 heating zones. The speed is 100 rpm and the throughput 8 to 10 kg/h.

The type, melt temperature, melt viscosity, and weight percentage of the synthetic fiber material; and the starch melt-spinnable composition type, extrusion temperatures, and color quality are all compiled in Table 1. The material properties of the resulting starch mixtures are given in Table 2.

The melt viscosities of the synthetic fiber materials (component B) are determined according to DIN 53 735 at 160° C. and 21.2N. The melt viscosities of the starch mixtures are measured by a modified melt-flow index method at 160° C. and 236.4N. The water content is determined according to Karl Fischer per DIN 53 714, the melting point is measured by differential calorimetry in the dry state at a heating rate of 20° C./min in a Du Pont Thermal Analyzer apparatus, Type 1091B.

In the Examples, the products used are as follows.

Grilon CF 62 BSE is a copolyamide based on the monomers PA-6 and PA-6.9 from EMS-CHEMIE having a melting point of about 136° C.

Grilon CR 9 is a copolyamide based on the monomers PA-6 and PA-12 from EMS-CHEMIE having a melting point of about 200° C.

Grilon CA 6E is a copolyamide based on the monomers PA-6 and PA-12 from EMS-CHEMIE having a melting point of about 130° C.

Grilamid ELY 60 is a copolyamide from EMS-CHEMIE based on lactam-12, polyetherdiamine, and dimerized fatty acid having a melting point of about 160° C.

Griltex 1 is a copolyamide from EMS-CHEMIE based on the monomers PA-6, PA-12, and PA-6.6 having a melting point of about 110° C. and a melt viscosity (DIN 53 735) of about 600 Pa.s (21.2N./160° C.).

Griltex 2 is a copolyamide from EMS-CHEMIE based on the monomers PA-6, PA-12, and PA-6.6 having a melting point of about 125° C. and melt viscosity (DIN 53 735) of about 400 Pa.s (21.2N./160° C.).

Griltex 3 is a copolyamide from EMS-CHEMIE based on the monomers PA-6, PA-12, and PA-6.6 having a melting point of about 110° C. and a melt viscosity (DIN 53 735) of about 500 Pa.s (21.2N./160° C.).

Griltex 4 is a copolyamide from EMS-CHEMIE based on the monomers PA-6, PA-12 and PA-6.6 having a melting point of about 110° C. and a melt viscosity (DIN 53 735) of about 100 Pa.s (21.2N./160° C.).

Griltex 5 is a copolyamide from EMS-CHEMIE based on the monomers PA-6, PA-12, PA-6.6, and PA-11 having a melting point of about 80° C. and a melt viscosity (DIN 53 735) of about 150 Pa.s (21.2N./160° C.).

CAPA 650 is a polycaprolactone from the firm Interrox.

TABLE 1

Examples	Type	Component (B)				Starch Content Example 1	T1 (°C.)	T2 (°C.)	T3 (°C.)	T4 (°C.)	T5 (°C.)	Tsch ³ (°C.)
		Melting point ¹ (°C.)	Melt Viscosity ² 21.2 N 160° C./Pa s	Percentage (parts by weight)								
2	Grilon CF 62 BSE	136	3100	50	50	0	140	145	145	145	145	167
3	Grilon CF 62 BSE	136	3100	40	60	0	140	145	145	145	145	163
4	Grilon CF 62 BSE	136	3100	30	70	0	140	145	145	145	145	161
5	Grilon CF 62 BSE	136	3100	20	80	0	140	145	145	145	145	157

TABLE 1-continued

Examples	Type	Component (B)					T1 (°C.)	T2 (°C.)	T3 (°C.)	T4 (°C.)	T5 (°C.)	Tsch ³ (°C.)
		Melting point ¹ (°C.)	Melt Viscosity ² 21.2 N 160° C./Pa s	Percentage (parts by weight)	Starch Content Example 1							
6	Grilon CF 62 BSE	136	3100	10	90	0	140	145	145	145	165	
7	Grilon CR 9	200	—	50	50	0	210	230	230	230	235	
8	Grilon CA 6 A	130	3600	50	50	0	140	140	140	140	165	
9	Grilamid ELY 60	160	—	50	50	0	150	170	150	150	179	
10	Grilamid ELY 60	160	—	30	70	0	150	170	150	150	180	
11	Grilamid ELY 60	160	—	10	90	0	150	170	150	150	178	
12	Grilamid ELY 60	160	—	5	95	0	150	170	150	150	179	
13	Griltext 1	110	600	50	50	0	150	150	130	130	151	
14	Griltext 1	110	600	40	60	0	150	150	130	130	145	
15	Griltext 1	110	600	30	70	0	150	150	130	130	147	
16	Griltext 1	110	600	20	80	0	150	150	130	130	149	
17	Griltext 1	110	600	50	50	0	150	150	130	130	147	
28	Griltext 1	110	600	10	90	0	150	150	130	130	153	
19	Griltext 1	110	600	5	95	0	150	150	130	130	153	
20	Griltext 2	125	400	50	50	0	150	150	130	130	150	
21	Griltext 2	125	400	20	80	0	150	150	130	130	153	
22	Griltext 3	110	500	50	50	0	150	150	130	130	143	
23	Griltext 4	110	100	50	50	0	150	150	130	130	143	
24	Griltext 5	80	150	50	50	0	120	100	105	100	125	
25	Griltext 5	80	150	80	20	0	100	100	110	120	126	
26	Griltext 5	80	150	60	40	0	100	100	110	120	130	
31	Griltext 5	80	150	40	60	0	100	100	110	120	128	
32	Griltext 5	80	150	30	70	0	100	100	110	120	131	
27	Capa 650	60	450	50	50	0	100	130	100	100	123	
28	Capa 650	60	450	30	70	0	150	170	150	150	164	
29	Capa 650	60	450	10	90	0	150	170	150	150	165	
30	Capa 650	60	450	5	95	0	150	170	150	150	165	

¹Melting point per DSC²Melt viscosity at 160° C. and 21.1 N according DIN 53 735³Tsch = Temperature of the melt

TABLE 2

Material Properties of the starch mixture										
Exam- ple	Water ¹ (wt. %)	Melting Point ² (°C.)	Melt visco- sity ³ (Pa s)	Modulus of Elasti- city ⁴ (N/mm ²)	Tenaci- ty ⁵ (N/mm ²)	Elonga- tion ⁶ (%)	Cold Water Swelling (%)	Hot Water Dis- solu- tion	Transpa- rency	Color
2a	11,60	—	259	78	10,5	434	max. 10	ja	nein	+
2b	4,40	107	1867	254	21,1	404	max. 10	ja	nein	+
3	2,20	111	4508	499	17,5	221	max. 10	ja	nein	+
4	1,80	115	6500	1038	26,6	4	max. 10	ja	nein	+
5	1,60	113	8000	1393	30,4	3	Auflosung	ja	nein	○
6	—	—	—	—	—	—	Auflosung	ja	nein	○
13	5,5	143	215	117	14,6	434	max. 10	ja	gut	+
14	7,65	145	255	71	13,0	520	max. 10	ja	gut	++
15	7,57	147	275	110	9,6	355	max. 10	ja	sehr gut	++
16	8,11	149	271	89	6,4	220	Auflosung	ja	sehr gut	++
17	5,59	147	263	—	—	—	max. 10	ja	gut	++
18	4,60	165	2840	190	9,3	64	Auflosung	ja	sehr gut	++
19	4,43	163	3575	160	8,2	66	Auflosung	ja	gut	○
20	7,60	146	265	75	14,0	510	max. 10	ja	sehr gut	++
21	8,05	148	283	92	7,5	210	Auflosung	ja	gut	++
22	—	—	—	—	—	—	max. 10	ja	gut	++
23	—	—	—	—	—	—	max. 10	ja	nein	++
24	—	—	—	—	—	—	max. 10	ja	nein	++
25	3,10	—	—	—	—	—	max. 10	nein	nein	++
26	3,30	—	—	—	—	—	max. 10	nein	nein	++
27	5,10	57	303	222	3,4	400	max. 10	ja	nein	++
28	8,10	58	152	142	6,1	77	Auflosung	ja	nein	++
29	3,50	163	5299	330	10,3	18	Auflosung	ja	nein	++
30	3,100	161	5772	270	n.g.	n.g.	Auflosung	ja	nein	++

¹Final water content according to DIN 53 714²Melting point according to DSC³Melt viscosity according to EMS, at 160° C. and 236.4 N⁴Tensile modulus of elasticity according to DIN 53 457^{5,6}according to DIN 53 455

Production of the fibers according to the invention

EXAMPLES 33 to 43

Selected melt-spinnable compositions from Examples 1 to 32 are adjusted to different water contents and processed into filaments on a compact melt spinning-drawing unit. The unit includes a BARMAG extruder ZE4 (screw size D25/24D), a gear pump, and an electrically heated spinning block. For spinning, a die packet is used which is designed for highly viscous melt compositions and includes a special pressure plate and distributor plate, as well as a 68-hole die plate of nozzle diameter 0.35 mm. The filaments issuing from the die plate are cooled into a waterbath at 20°–23° C., drawn off over three heated twin rollers and drawn, and then conducted over an unheated fourth twin rollers to a winder.

In Example 43, a fatty acid ester (Mold-Wiz) is used instead of water for cooling the filaments.

In Example 44, monofilaments from the starch mixture of Example 26 are produced. For this, the throughput is increased, a 6-hole spinnerette plate (nozzle diameter 0.80 mm) is used, the threads are conducted separately over the drawing units, and wound individually onto spools. The resulting monofilaments have a diameter of 0.27 to 0.28 mm, a tenacity of 1.2 cN/dtex, and an elongation of 37%. The various water contents and test results are set forth in Table 3.

TABLE 3

Manufacturing parameters and test data of the fibers according to the invention										
Fila- ment Example No.	Molding compo- sition Example No.	Water content %	Spin- ning Tempe- rature °C.	Roller Temperature °C.	Total Drawing Ratio 1:	Win- ding Speed m/min.	Filament Data			
							Count dtex	Tena- city cN/dtex	Elonga- tion %	
33	3	2.3	140	62/63/64/24	3.22	116	3710	0.6	32.5	
34	8	1.8	158	74/75/105/25	3.55	160	2700	1.0	29.4	
35	15	2.2	152	68/68/90/24	3.25	240	1790	0.8	24.2	
36	20	2.5	148	60/62/70/22	4.50	200	2150	1.3	31.5	
37	25	2.1	143	60/62/65/23	5.50	215	2000	2.2	57.2	
38	26	1.4	137	59/62/64/23	5.30	215	2000	1.5	40.1	
39	24	1.4	137	61/60/65/23	5.10	215	2000	1.4	29.8	
40	31	2.3	136	60/60/65/22	4.88	215	2000	1.2	24.5	
41	32	2.2	138	60/61/65/22	3.50	160	2680	0.7	26.1	
42	28	1.4	116	22/23/24/22	4.25	180	2430	0.9	22.0	
43	1	6.0	136	50/54/55/23	2.40	120	3800	0.5	16.0	
44	26	1.4	136	60/63/63/23	5.50	116	883	1.3	33.5	

EXAMPLE NO. 45

The starch mixture of Example 24 is used for rapid spinning. The granulate with a water content of 1.4% is melted in a BARMAG 3E8 extruder (screw size D30/30D), forced, at a spinning temperature of 146° C., through a die packet with a 34-hole spinnerette plate of nozzle diameter 0.35 mm, and the resulting threads are cooled by a cross current of the air. The threads are then oiled with spin finish, drawn off over a roller with idler roller at 2520 m/min, interlaced, and wound onto a spool at 2500 m/min. The resulting multifilament of titer dtex 190/34 shows a tenacity of 1.4 cN/dtex at an elongation of 46%. This multifilament is suitable for draw texturing to form textured yarn.

EXAMPLE 46

The starch mixture of Example 24 is used for spin-stretching. Spinning, cooling, and oiling are carried out in

accordance with Example 45. The filaments are then guided over 5 rollers with idler rollers running at the following speeds and temperatures: 1625 m/min/unheated; 1650 m/min/55° C.; 2600 m/min/60° C.; 2750 m/min/65° C., and 2700 m/min/27° C. The spin-drawn thread is wound at 2600 m/min. It shows a count of dtex 170f34, a tenacity of 1.6 cN/dtex, and an elongation of 25.5%.

EXAMPLE NO. 47

The multifilaments of Example 40 are bundled at a speed of 120 m/min to a total titer of 2000 tex, conducted through a stuffer box for crimping, dried continuously at 70° C. in an apron conveyor drier, and cut in a FLEISSNER cutting machine to a length of 80 mm. These staple fibers of a titer of 30 dtex exhibit a tenacity of 1.4 cN/dtex and an elongation at rupture of 27%. This example shows that such starch mixtures can be processed in a single-stage using a compact spin-drawing unit to form staple fibers.

EXAMPLE 48

The starch mixture of Example 24 is processed to form staple fibers according to the two-stage spin and drawing method. The granulate of Example 24 is melted in a BARMAG 6E4 extruder and forced at a rate of 877 g/minute through a spinnerette packet with a 210 mm diameter spinner-

ette plate having 645 holes, each with a nozzle diameter of 0.40 mm. The spun threads are cooled by a transverse current of air and a spin finish is applied thereto. The threads are guided over 4 rollers in an open loop to the can where they are deposited at a rate of 680 m/minute. The count of the spun cable is tex 1290f645.

The spun fibers are drawn simultaneously from 3 of these cans and guided together through a 0.5% solution of finisher in water. They are then guided over 3 drawing units having 2 rollers each, at rates and temperatures of 56.0 m/minute/58° C., 103 m/min/60° C., and 100.5 m/minute/unheated.

Subsequently, they are wetted in a brightening device containing a 3% finish solution, crimped in a crimping chamber, dried at 70° C. in an apron conveyor drier, and cut in a fiber cutter to a fiber length of 80 mm. The resulting crimped staple fiber has a single titer of 11.0 dtex, a tensile strength of 1.5 cN/dtex, and an elongation at rupture of 31.5%.

EXAMPLE 49

Fibers of component (A) without component (B):

Using the process described in Example 1, a starch molding composition which was subsequently granulated, was produced from 70 parts by weight hydroxypropyl corn starch having a degree of substitution of 0.06 and an amylose content of 85% by weight as well as 15 parts by weight of glycerol, 13 parts by weight of sorbitol, 2 parts by weight of urea, and 5 parts by weight of the processing aid "Paraloid K125/175" 3:2. This starch molding composition with a water content of 7.7% by weight was melt-spun according to Example 44 at a spinning temperature of 136° C. on a spinning installation as described in Examples 33 to 43, but having now according to Example 44 a spin pack with 6 hole and nozzle diameters of 0.8 mm. The resulting elementary threads were cooled with air, conducted separately over the stretching groups and spooled singly.

Using godet temperatures of 50/55/55/25° C., a drawing ratio of 1:1.79 and a rate of 15.3 m/min, the resulting monofilaments or threads had a diameter of 0.40 mm, a tensile strength of 0.24 cN/dtex and an elongation at break of 85%.

While only a limited number of specific embodiments of the present invention have been expressly disclosed, it is, nonetheless, to be broadly construed and not to be limited except by the character of the claims appended hereto.

What we claim is:

1. Rapidly biodegradable fibers produced by a melt-spinning process and comprising
 - A. 20 to 95 parts of a melt-spinnable composition comprising
 1. 56 to 96 parts of at least one modified starch,
 2. 4 to 40 parts of a destructuring agent, and
 3. 0 to 4 parts of at least one additive selected from the group consisting of urea, emulsifiers, lubricants, proteins, and alkali salts of proteins, components 1, 2, and 3 totaling 100 parts; and
 - B. 80 to 5 parts of at least one melt-spinnable polymer having a melting or softening point of 50° to 220° C. selected from the group consisting of aliphatic polyamides, aliphatic polyesters and homo- and copolyamides of omega amino carboxylic acids and lactams.
2. The fibers of claim 1 wherein said component 1 is 10 to 100 parts, component 2 is 90 to 66 parts, component 3 is 10 to 30 parts, and component B is 80 to 5 parts, said at least one additive being selected from the group consisting of urea, emulsifiers, and lubricants.
3. The fibers of claim 1 wherein said destructuring agent comprises a plasticizer.
4. The fiber of claim 1 wherein said additive is 0.1 to 2.0 parts of urea and 0.1 to 2.0 parts of at least one emulsifier.

5. The fibers of claim 1 wherein said starch has a natural water content of 5% to 16%.

6. The fibers of claim 1 wherein said starch has an amylose content of 20% to 100%.

7. The fibers of claim 1 wherein said starch has been modified by reaction of its OH groups with at least one substance selected from the group consisting of ether-, ester-, urethane-, carbamate-, and isocyanate-forming substances.

8. The fibers of claim 7 wherein said starch is a hydroxy-alkyl, acetyl, carbamate starch or a mixture thereof, said alkyl having 2 to 6 carbon atoms.

9. The fibers of claim 7 wherein said starch has a substitution degree of 0.01 to 3.0.

10. The fibers of claim 7 wherein said starch is starch acetate and said substitution degree is 2.0 to 3.0.

11. The fibers of claim 1 wherein said destructuring agent comprises a plasticizer which is at least one organic compound having at least one hydroxyl group.

12. The fibers of claim 1 wherein said at least one additive comprises 0.1 to 1 part of an emulsifier.

13. The fibers of claim 1 wherein said emulsifier has an HLB value of 0 to 20.0.

14. The fibers of claim 1 wherein said at least one additive comprises 0.1 to 2 parts of urea.

15. The fibers of claim 1 wherein said melt-spinnable polymer has a melt flow index (MFI) of 10 to 10,000 Pa.s at 21.2N and a temperature of 30° C. above said melting or softening point.

16. The fibers of claim 1 wherein said melt-spinnable polymer is at least partially biodegradable, itself or in homogeneous mixtures with starch.

17. The fibers of claim 1 wherein said melt-spinnable polymer is at least one polyamide.

18. The fibers of claim 1 wherein said melt-spinnable polymer is selected from the group consisting of polyhydroxybutyrates, polyhydroxyvalerates, polycaprolactone, polyesters, and mixtures thereof.

19. The fibers of claim 17 wherein said polyamide is a homo- and/or copolyamide derived from omega-amino carboxylic acids having 2 to 12 carbon atoms, lactams having 4 to 12 carbon atoms, and/or from the reaction of diamines having 2 to 12 carbon atoms with dicarboxylic acids having 2 to 12 carbon atoms.

20. The fibers of claim 1 further comprising a branching or cross-linking agent.

21. The fibers of claim 20 wherein said branching or cross linking agent is selected from the group consisting of isocyanate-, formaldehyde-, epoxy-, anhydride-, ether-, ester-, amide-forming groups, and mixtures thereof.

* * * * *

[54] **PROCESS FOR THE PRODUCTION OF
PAPER CONTAINING STARCH FIBERS AND
THE PAPER PRODUCED THEREBY**

[75] Inventors: **Henry R. Hernandez**, Somerville;
Donald S. Greif, Bound Brook;
Albert N. Barna, Plainfield, all of
N.J.; **Douglas S. Thornton**, Himsdale,
Mass.

[73] Assignee: **National Starch and Chemical
Corporation**, Bridgewater, N.J.

[*] Notice: The portion of the term of this patent
subsequent to Feb. 13, 1996, has been
disclaimed.

[21] Appl. No.: **842,543**

[22] Filed: **Oct. 17, 1977**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 670,360, Mar. 25,
1976.

[51] Int. Cl.³ **D21H 5/12**

[52] U.S. Cl. **162/141; 162/145;
162/146; 162/157 R**

[58] Field of Search **162/146, 157 R, 175,
162/141, 142, 176, 145; 264/184, 186, 185;
106/210, 213, 217; 127/33**

[56] **References Cited**

U.S. PATENT DOCUMENTS

1,682,293	8/1928	Lilienfeld	264/187
2,570,449	10/1951	Horsak	264/186
2,792,765	5/1957	Kerridge et al.	162/141
2,902,336	9/1959	Hiemstra et al.	264/186
3,114,672	12/1963	Schott	162/146
3,116,351	12/1963	Wohlraabe et al.	264/186
3,293,057	12/1966	Rumberger	106/213
3,839,144	10/1974	Louden	162/141

FOREIGN PATENT DOCUMENTS

847431 4/1960 United Kingdom 264/186

OTHER PUBLICATIONS

"Freeness Scale Interconversion" TAPPI Data Sheet
(1945).

Primary Examiner—Peter Chin

Attorney, Agent, or Firm—James & Franklin

[57] **ABSTRACT**

A process for the production of paper and paperboard is disclosed wherein water-insensitive starch fibers, produced by extrusion of a starch dispersion into a coagulating solution, are employed to replace all or part of the cellulosic or other pulp conventionally employed. There is also disclosed a method for the incorporation of functional additives into paper during the production thereof; and a method for binding fibers in non-woven webs.

18 Claims, No Drawings

PROCESS FOR THE PRODUCTION OF PAPER CONTAINING STARCH FIBERS AND THE PAPER PRODUCED THEREBY

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part application of Ser. No. 670,360 filed Mar. 25, 1976.

BACKGROUND OF THE INVENTION

I. Field of the Invention

This invention is directed to a process for producing paper using water-insensitive starch fibers to replace all or part of the cellulosic or other pulp conventionally employed, and to the paper produced thereby. The invention also relates to a novel method for the production of certain specialty papers, as well as to methods for the incorporation of functional additives into paper during the production thereof and for binding fibers in non-woven webs.

II. Brief Description of the Prior Art

Various natural fibers (other than cellulose) as well as a variety of synthetic fibers have been employed in making paper, however, all these replacements have failed to provide a commercially acceptable substitute for cellulose due to their cost, poor bonding properties, chemical incompatibilities, difficulty in handling in papermaking systems, etc. While it has also been suggested to use starch fibers in various aspects of the papermaking process, commercial attempts to use such fibers have not resulted in any degree of success and paper is still being manufactured almost completely from wood-based cellulosic ingredients—the supply of which is being rapidly depleted.

It is apparent that the aqueous systems normally employed in the paper making operations require pulp fibers possessing sufficient water-insensitivity that they can be used in all aspects of the manufacturing process throughout a relatively wide pH range without losing their integrity. In this regard, the few references which suggest the replacement of starch fibers for cellulose fibers (e.g. U.S. Pat. No. 1,682,293) require chemical modification of the starch in order to radically change its naturally occurring properties prior to forming the fiber so as to provide the degree of water-insensitivity required in the papermaking process. Alternatively, other references (e.g., U.S. Pat. No. 2,570,449) require that the papermaking process itself be modified as by replacing the conventionally employed aqueous system with an alcohol solvent in which the starch fibers are not soluble. It will be recognized that the use of such techniques is both impractical and uneconomical when employed on a commercial basis.

As another aspect of the papermaking operation, it is often necessary to incorporate additives into the pulp in order to achieve specific end properties. Thus, additives such as pigments, latices, synthetic microspheres, fire retardants, dyes, perfumes, etc. are often employed in the manufacture of paper. The efficient retention of these additives at the wet end of a paper machine presents difficulty to the manufacturer since that portion which is not retained creates not only an economic loss, but also a significant pollution problem if it becomes part of the plant effluent. Furthermore, such additives are also added via coating or saturation processes commonly known in the art. These processes usually require that excess heating energy be consumed to re-dry the

paper after coating. Moreover, in some instances the coating systems are required to be solvent based which then creates extreme capital expense and requires regulation to recover volatile materials.

It is therefore an object of the present invention to provide a commercially viable process for the use of starch fibers as a partial or complete replacement for cellulose in conventional papermaking operations.

It is also an object to provide a process which efficiently enables the retention and incorporation of additives into paper during the manufacture thereof.

It is a further object to provide a process which enables water-insoluble additives to be introduced into the paper as fiber encapsulated additives.

Another object is to provide ordinary and improved specialty papers according to such process.

A further object of the invention is to provide an efficient and economical process for binding synthetic and/or natural fibers in non-woven web form.

These and other related objects will be apparent from the description which follows.

SUMMARY OF THE INVENTION

In accordance with the present invention, it has been found that the above and related objects are attained when water-insensitive starch fibers, produced by the precipitation of a colloidal dispersion of starch in a coagulating salt solution, are employed as partial or complete replacements for cellulose and similar fibers in conventional paper and paperboard manufacturing operations. The fibers may be used to extend the pulp, as a means for incorporating additives into the paper product, as binder for the fibers in non-woven webs or for any combination thereof.

As used herein, the term "paper and paperboard" includes sheet-like masses and molded products made from fibrous cellulosic materials as well as such fibrous materials as may be derived from synthetics (such as polyamide, polyester, rayon and polyacrylic resin), mineral fibers (such as asbestos and glass), and the like.

As used herein, the expression "conventional papermaking operation" means the process of introducing an aqueous slurry of wood cellulose fibers (which have been beaten or refined to achieve a level of fiber hydration and to which a variety of functional additives can be added) onto a screen or similar device in such a manner that the water is removed, thereby forming a sheet of the consolidated fibers which, upon pressing and drying, can be processed into dry roll or sheet form. Also included within the scope of this expression are the conventional processes for the production of wet and dry-laid non-wovens.

Thus, in one aspect the present invention provides a feasible, efficient and economical process for extending existing raw material sources. Further, it allows the paper manufacturer a far greater degree of flexibility in his operations: he is able to obtain starch fibers in dry or wet-slab form and store them for subsequent use or he may incorporate the starch fiber manufacturing process into his plant as an integrated step in his plping and/or papermaking operations.

Moreover, the present invention offers the manufacturer a new means for incorporating additives into paper products with increased retention and consequently less economic loss and fewer pollution problems. As previously discussed, it is common practice in the manufacture of paper to introduce additives in con-

junction with the fibers used in the pulp. Such additives are incorporated in order to achieve specific paper properties other than what is contributed by the fiber itself. Such additives include materials which function as pigments (titanium dioxide, for example) as well as other materials introduced into paper to achieve such properties as improved brightness, opacity, smoothness, ink receptivity, fire retardance, water resistance, increased bulk, etc. As an additional embodiment of the present invention, it has been found that when starch fibers are produced so as to contain various functional additives, and such fibers are then utilized in the aqueous paper making process, retention of the additives is greatly increased when compared with that achieved using current methods. In addition to the increased retention, a further advantage of the addition of additives in this manner is the fact that there is no necessity for relying upon the sensitive charge balance relationship between the cellulose fiber additive and the flocculant (e.g., alum) or other retention aids. Indeed, it is unnecessary to use a flocculant or retention aid with the starch fibers used in the present invention.

It has also been found that non-woven webs can be produced in wet or dry-laid form in accordance with the present invention wherein starch fibers are incorporated within the web to serve as binders therefor. The starch fibers may be retained in the final web or, if the base fiber employed in the web is non-combustible, may be removed, depending upon the desired end use.

Specifically, the present invention is directed to an improvement in a process for manufacturing paper and paperboard comprising the steps of introducing an aqueous slurry of a fibrous pulp material onto a screen in such a manner that the water is removed thereby forming a sheet of consolidated fibers which, upon pressing and drying, yields the final paper product. The improvement comprises the step of replacing from 1 to 100% by weight of the pulp with water-insensitive starch fibers of 10 to 500 microns in diameter produced by extruding a thread-like stream of a colloidal dispersion of the starch, at 5 to 40% by weight solids, into a moving coagulating bath comprising an aqueous solution of a coagulating salt selected from the group consisting of ammonium sulfate, ammonium sulfamate, mono-basic ammonium phosphate, di-basic ammonium phosphate and mixtures thereof, the solution containing the coagulating salt in an amount at least sufficient to coagulate the starch.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The process of the present invention may readily be adapted to be used on any conventional paper making equipment using the procedures commonly used in the specific plant, with the only difference residing in the substitution of starch fibers for all or part of the cellulose pulp.

The starch fibers employed may be produced using a number of variations, the only requirement being that the waterinsensitive fibers have a diameter of 10 to 500 microns and that they be precipitated by the extrusion of a thread-like stream of a colloidal dispersion of starch at 5-40%, by weight solids, into a suitable moving coagulating salt solution.

Fibers may be employed which are produced from any naturally occurring or fractionated starch. Thus, corn starch, waxy maize, rice, tapioca, wheat, potato, high amylose corn starch, commercial amylose powder,

etc. may be employed with naturally occurring corn starch, tapioca and waxy maize being preferred due to their economy and availability.

The concentration of the starch solids in the dispersion should be about 5 to 40% by weight. While higher concentrations of starch solids may be used, the resulting dispersions become very viscous and special equipment is required to handle them. The particular concentrations employed in the dispersions will however, affect the properties of the final fiber and the desired end use. As an example, starch fibers prepared from 5% solids dispersions have been found to be particularly useful in the production of glassine or greaseproof papers while starch fibers prepared from 15% solids dispersions have been found better suited for use in more porous papers such as filter paper.

The particular starch employed must be used in the form of a colloidal dispersion. For the purposes of this invention, the term "colloidal dispersion" means dispersion of starch which is substantially free of granules and which exhibits, on standing at the temperature at which it is to be used, little evidence of gelation or precipitation. This state of dispersion may be obtained using a variety of techniques depending upon the particular starch base employed, the desired end use and the equipment available.

When native starches that are very high in amylopectin content, such as waxy maize, are employed, a suitable colloidal dispersion may be prepared merely by thoroughly cooking the starch in water with no chemical additives or modifications required. In most cases where starches which contain less than about 95% amylopectin are employed, it will be desirable to chemically derivatize or modify the starch to ensure its colloidal dispersion before adding it to the aqueous system. The derivatization or modification is carried out to an extent which will insure the production of the desired colloidal dispersion without affecting the ability of the starch to subsequently precipitate. Alternatively, if there is no objection to the presence of caustic in the system, the latter starches may be dispersed in aqueous sodium hydroxide, potassium hydroxide or other common alkali. As further alternatives, the starch bases may also be dispersed in a minor amount of an organic solvent such as dimethylsulfoxide and then added to water, or the starch base may be dispersed in conjunction with chemical additives such as urea and/or paraformaldehyde. In the cases where causticizing is employed, the amount of alkali used must be sufficient to adequately disperse the starch. Typical amounts of alkali used when sodium hydroxide is employed are from 15 to 40%, by weight, based on the weight of the starch.

In preparing the starch dispersion, the starch is added to the dispersing medium and vigorously agitated until a state of colloidal dispersion is achieved. In the case of dilute dispersions of starch (i.e. about 5-10% starch solids by weight), this will require about 45 minutes, with longer periods and/or moderate heat required for more concentrated starch dispersions or for certain chemically modified starch bases.

Most of the starch dispersions, including those of waxy maize and most of the chemically modified starches, may be cooled to room temperature prior to introduction into the coagulating bath. In the case of a few of the less chemically modified starches, it will be preferred to employ the dispersions at approximately the elevated temperatures at which they are prepared so

as to maintain the necessary colloidal dispersion and to insure efficient fiber production.

The coagulating bath used in preparing the starch fibers employed in the present invention comprises an aqueous solution containing specific ammonium salts selected from the group consisting of ammonium sulfate, ammonium sulfamate, mono- and dibasic ammonium phosphate and mixtures thereof. It is also possible to combine the above-mentioned functional salts with other compatible salts which will form a starch precipitate so as to obtain satisfactory coagulation and a fibrous product. Suitable salts for this purpose include ammonium persulfate, ammonium carbonate, ammonium bromide, ammonium bisulfite, ammonium nitrite ammonium nitrate, ammonium bicarbonate, ammonium oxalate, sodium and potassium chloride, sodium and potassium sulfate, among others. Generally, no advantage is seen in using these additional salts since the ammonium sulfate, sulfamate or phosphate salts must still be present in their respective minimum amount in order to effect coagulation. The only instances where the presence of substantial amounts of other salts may be desirable is in the use of the recycled coagulation bath wherein salts are present which have been generated in situ, as will be discussed hereinbelow.

The minimum concentration of the salt required to effect coagulation as well as the preferred salt or salt blend will vary depending upon the particular starch base employed. For example, in the case of waxy maize starch, it is necessary for ammonium sulfate to be present in amounts of at least 35%, by weight of the total solution, ammonium sulfamate 72% (saturation), dibasic ammonium phosphate 37% and mono-basic ammonium phosphate 40%. In the case of corn starch or similar starches containing about 64-80% amylopectin, lower concentrations of salt may be used with ammonium sulfate required in amounts of 20%, ammonium sulfamate 50%, mono-basic ammonium phosphate 25% and di-basic ammonium phosphate 30%. In the case of hybrid corn starches containing less than about 50% amylopectin, ammonium sulfate must be present in amounts of at least 15%, ammonium sulfamate 40%, di-basic ammonium phosphate 25% and mono-basic ammonium phosphate 20%.

It will be recognized that alkali salts are generated in the coagulating bath when causticized starch dispersions are employed, with satisfactory production of the desired starch fibers continuing until the level of the generated salt is relatively high. The generated salt tolerance level above which production of the fibers becomes inefficient will vary depending upon such factors as the specific salt employed, the total salt solids employed, the starch solid concentration in the dispersion, the amount of amylopectin in the starch base, etc. Once this salt tolerance level is determined, a steady-state system may be achieved at this maximum level (or less) by the periodic addition of ammonium sulfate on a continuous basis. As an example, when sodium hydroxide is used as a dispersing medium and the starch mixture is extruded into an ammonium sulfate coagulating bath, sodium sulfate is generated. In this case, it has been found that production of corn starch fibers (13% solids dispersion) will continue at a satisfactory level until a maximum of about 70 parts sodium sulfate per 30 parts ammonium sulfate (44% solids solution) is present in the bath. Above this level of sodium sulfate, production of the starch fibers becomes less efficient and the resulting fibers tend to lose their individual integrity.

However, by adding a small amount of an inorganic acid to the initial coagulating bath or to the bath during formation of the fibers, the level of the generated salt in the system may be appreciably raised before production of the fibers is seriously affected. Thus, using the example discussed previously, the addition of as little as 3 parts of sulfuric acid per hundred parts of the initially charged coagulating bath salt results in a tolerance level of 90 parts sodium sulfate per 10 parts ammonium sulfate thereby increasing the longevity of the coagulating bath.

It is apparent that the salt solution used in the fiber forming process may be recycled and used again once the fibers have been removed. It is, however, important that the salt concentration be maintained, especially where the salt is being depleted through a chemical reaction involving the starch dispersion as it is introduced. In this regard, the starch dispersions which do not contain caustic present little difficulty in recycling other than that the solids content of the salt be maintained. However, in those cases where causticized starch dispersions are employed, chemical reactions with the coagulating solution will occur. For example, if ammonium sulfate is used, the reaction results in the formation of ammonium gas and sodium sulfate. The recycling of such a system can be extended by recovering the ammonia in an acid scrubber and returning it to the system as ammonium sulfate. The generated sodium sulfate can be used in the coagulating bath as part of the salt blend until the tolerance levels discussed previously are attained or can be used as a raw material in other aspects of the pulp or papermaking operation, e.g. as a source of "salt cake" in the production of Kraft pulp.

Starch fibers can be produced at any temperature at which the starch dispersion can be handled. Generally, the coagulation bath is maintained at about room temperature (20° C.) during production of the fibers, however, temperatures as high as about 70° C. may be used. These higher temperatures may be desired under certain conditions since they increase the solubility of the salt in the coagulating bath resulting in more concentrated solutions. Thus, when it is desired to produce waxy maize fibers using mono-basic ammonium phosphate as coagulant, it is desirable to increase the temperature of the bath so as to obtain a concentration of salt of approximately 40% (saturation level for the mono-basic ammonium phosphate at 20° C. is 28%).

In preparing the starch fibers used in the invention, the starch dispersion is introduced continuously or by drops in the form of a thread-like stream into the moving coagulating salt solution. This introduction may be accomplished either from above or below the salt solution using any conventional techniques. Thus, the dispersion may be extruded through an apparatus containing at least one aperture, such as a spinnerette, a syringe or a biuret feed tube. Alternatively, the dispersion may be discharged under pressure from a pipe or tube containing a plurality of apertures into a surrounding enclosed area, e.g. a concentric pipe, containing the moving coagulating solution. Various adaptations of the above and related techniques may be used and the fibers may be thus produced using either batch or continuous operations.

In accordance with either embodiment, the aqueous salt coagulating solution should be moving when the starch dispersion is introduced and the directionality of the two flows can also be utilized in controlling fiber lengths and diameters or widths. Thus, if the salt solu-

tion is moving in a direction generally concurrent with the flow of the starch dispersion, rounder fiber lengths are formed; if the starch dispersion is introduced at an angle of about 90° to the flow of the salt solution, relatively flatter fibers are formed. Generally apertures of 10 to 500 microns in diameter are preferred, in order to produce fibers of the size required herein. Thus, the starch fibers used in the present invention have diameters (widths) of 10 to 500 microns and will generally have lengths of from about 0.1 to 3.0 mm. if they are to be used as cellulose pulp replacements in paper. For non-woven application, fibers of longer lengths may be employed.

It will be recognized that the length, cross-sectional size and configuration of the resultant fibers are dependent upon a number of interrelated parameters in addition to those described hereinabove. Thus, the viscosity, the solids content of the starch dispersion, as well as the particular components used in the coagulating solution and/or starch dispersion and the relative flow viscosities thereof are additional factors which can be used in conjunction with the parameters discussed previously in order to control the dimensions of the resultant fiber.

This and similar coagulating processes producing starch fibers useful herein are described in our co-pending patent application Ser. No. 670,342 filed on even date herewith, now U.S. Pat. No. 4,139,699 the disclosure of which is included herein by reference, as well as in U.S. Pat. No. 2,902,336. Various modifications of the processes may also be employed as long as the final fiber possesses sufficient water insensitivity to be employed in the papermaking operation.

The resulting aqueous slurry or suspension of starch fibers may be used directly by introducing it into the pulp stream thereby enabling production of fibers and paper web "inline" in the paper manufacturing plant. If this embodiment is to be used, it is generally preferred to first wash the fibers free of coagulating salt prior to introducing the slurry into the paper manufacturing operation. Alternatively, the fibers may be recovered in the dry state by collecting from water on a screen or similar device. It is then preferably to reslurry the fibers into a non-aqueous solvent such as methanol, ethanol, isopropanol, acetone or the like in which the fibers are not soluble. The fibers are then recovered, as by filtration, from the solvent and dried. Other methods such as centrifuging, flash-drying or spray-drying may also be used to remove the water. Once dried, the fibers may be re-introduced into an aqueous medium and will exhibit excellent re-dispersibility maintaining their discrete, discontinuous structure. Alternatively, the fibers may be recovered from the slurry, as by filtration, washed and placed in water at levels of up to about 50% solids and formed into "wet-slabs" for subsequent use.

It is also to be noted that the starch employed may be chemically treated to vary the properties of the fiber produced or to help effect formation of the colloidal dispersion. Alternatively, the starch fibers may be treated after formation in order to produce certain functional characteristics. Thus, the starch may be chemically treated, as by aminoethylation, in order to provide rapid dispersibility of the starch in the dispersion, which treatment will also result in the production of a fiber which possesses a cationic charge when employed in an aqueous medium. Similarly, a starch may be used which is modified to contain anionic groups so as to be stable in a dispersion and which, after regeneration, will produce a fiber having anionic properties. The fibers may

also be modified after their formation in order to achieve specific functional properties. Thus, improved anionic functionality might be obtained by bleaching the fibers after precipitation as long as the conditions are not so severe as to destroy the fibers. The properties of the fibers may also be controlled by using blends of modified and unmodified starches or by the addition of other functional materials, such as polyacrylic acid, to obtain the specifically desired properties.

As one of the advantages of the method of the present invention there is provided a means to improve paper products in a variety of manners due to the properties which are either inherent in or which may be imparted to the starch fiber itself. As an example of such improved properties, we may consider the production of such diverse specialty papers as glassine paper and filter paper which require special treatment when conventionally produced.

Glassine paper is made from pulps in which the quality of the fiber permits a high degree of hydration. It is the mechanical treatment of the pulp while suspended in water that causes the distinctive greaseproof properties. The fibers are fibrillated and swollen to an almost gelatinous condition. When paper is made from hydrated fibers, a dense non-porous sheet is formed on the wire. The resultant sheet is resistant to the penetration of greases and oils because it is composed of nearly continuous well hydrated cellulose. To get the cellulose in this well hydrated form requires a considerable amount of energy. Glassine manufacturers must subject their stock to refining for extended periods of time or increase the number of refiners through which the stock must pass. Once the stock is hydrated and introduced on the wire it drains very slowly. As a result, machine speeds are limited to between 150-500 fpm depending somewhat upon the basis weight of the paper. The stock temperature may be elevated with steam to accelerate water removal on the wire. Attempts by glassine manufacturers to use cationic polyelectrolytes for improving drainage has met only limited success. The flocculation of the fibers may improve drainage but this disruption in formation can cause pinholes which reduce oil and greaseproof properties of the product.

We have now found that when starch fibers are combined with cellulose fibers which have been beaten to a degree less than would be required in conventional glassine manufacture, the resultant mixture has a significantly higher freeness and will drain at lower temperatures in about one-third the time usually required at the elevated temperatures presently used, with higher wet mat solids after pressing and improved drying efficiency relative to the conventional glassine stock. Moreover, the resultant sheet properties of this novel paper exhibits greater internal strength (Z-directional strength), improved oil holdout properties and greater resistance to the passage of air relative to conventional glassine paper. It is apparent that the reduction of the cellulose refining requirements can result in significant energy savings since the fiber mix need not be elevated in temperature to achieve acceptable water removal rates as is common practice in conventional glassine manufacture.

Starch fibers may also be employed to provide a more porous sheet which is a property that can be desirable in such papers as filter or saturating grades. In prior art methods, reduced refining of cellulose has been found to aid the development of this property, but does so only at the expense of weaker web strength. The incorporation of starch fibers according to the present inven-

tion, in conjunction with the cellulose, can result in a more porous sheet structure while maintaining, and often improving, the required strength properties.

As a further feature of the invention it is possible to incorporate certain hydrocolloids in the dispersing medium and to extrude the hydrocolloids together with the starch in order to produce a starch-hydrocolloid fiber which may be used in the papermaking process of the present invention. In order to achieve this fiber composition, it is only necessary that the hydrocolloid (in minor amounts, i.e. less than 50% by total solids weight), together with the starch portion, be placed in a state of colloidal dispersion prior to contact with the coagulating bath. Thus, in the case of water-dispersible hydrocolloids such as polyvinyl alcohol, carboxymethylcellulose, hydroxyethylcellulose, etc., it is only necessary to add the hydrocolloid to the water in which the starch is dispersed. In the case of other hydrocolloids, such as casein, it will be necessary to causticize the dispersion in order to form the colloidal dispersion required.

As an alternative embodiment of the present invention, water-insoluble additives may be uniformly admixed throughout the starch dispersion and subsequently encapsulated within the resultant starch fiber. Thus, water-insoluble additives, including pigments, metallic powders, latices, oils, plasticizers, microspheres (glass beads, foamed silica or other low density materials either in blown or unblown form), etc., may be encapsulated within the starch fibers of the invention. In a similar manner, water-insoluble synthetic polymers or latices, such as polyvinyl acetate, polyacrylonitrile, polystyrene, etc., may be incorporated within the fiber. It will also be noted that the density of the starch fibers may be varied by incorporating air or other gases in the starch dispersion prior to passing it into the coagulating bath.

It is to be further noted that certain water-soluble solid additives may also be co-extruded with the starch fibers. In such cases, the additive will be dissolved in the aqueous starch dispersion and the coagulating bath which is employed in forming the starch fibers will be adjusted by the addition of a sufficient quantity of a compatible salt capable of precipitating the additive. As an example, a commercial rosin size can be added to the starch dispersion and extruded into a coagulating bath containing the functional starch-coagulating salt together with sufficient aluminum sulfate to precipitate the rosin, thereby forming a co-precipitated starch-aluminum rosin fiber.

The water-insolubility of the starch fibers of the present invention can be further enhanced by the incorporation of conventional cross-linking agents, such as urea-formaldehyde, glyoxal, urea-melamine-formaldehyde, Kymene (registered tradename of Hercules, Inc., Wilmington, Delaware), etc. These crosslinking agents may be incorporated into the starch dispersion prior to extrusion or may be post-added to the starch fiber.

Generally, any additives employed will be used in amounts less than about 50% by weight of the total solids, however, certain additives including clay and pigments may be incorporated at levels up to about 80% by weight. It will be realized that the specific additive selected for incorporation, as well as the amount employed in any of the above-described embodiments, will depend upon what properties are desired in the final fiber. Thus, pigmented fibers show improved opacity and may be incorporated by conventional methods into

the fibrous web with overall improved pigment retention relative to that obtained by merely adding pigment to a paper stock system. Fire retardant properties may be conveyed to a substrate by incorporating polyvinyl chloride powder and antimony trioxide or other fire retardant chemicals within the starch fiber. Starch fibers containing microspheres may be incorporated into paper webs at high levels of retention. The retention of such spheres enables the production of sheets of high bulk and low weight as compared with cellulose sheets of comparable weight. In conventional sheets containing microspheres, the presence of the microspheres between the fibers has a debonding effect on the fibers and this results in a sheet of low strength. In contrast, the sheets of the present invention possess excellent strength properties as the spheres are encapsulated within the starch fibers so that the debonding effect on the spheres is minimized. The density of the starch fibers, and resultant paper, may also be varied by the incorporation of air or other gases in the starch dispersion prior to passage into the coagulating bath.

Furthermore, by using additive encapsulating fibers it will be possible, not only to provide a novel process of incorporating additives in paper, but also to produce novel effects in the paper itself. As an example, there are papermaking machines that produce a final web which is constructed of individual layers compressed together. Such equipment may be described as cylinder machines or Fourdriniers with a second down-line headbox or with multiple headboxes. Machines of this type normally use lower quality fibers for the inner plies and quality pulp as the top liner. By utilizing a pigmented starch fiber in the top line, production of paper web having the surface properties of coated board is possible. In essence a coated board would be produced via a wet-end application process due to the high concentration of starch and pigment at the substrate surface. Alternatively, special decorative or construction paper could be manufactured having different colored sides. Dyed fiber could be prepared at various colors and fed to two different headboxes. Such twocolored sided paper is prepared today but requires the use of surface applications during processing.

One of the advantages of the use of water-insoluble synthetic polymers encapsulated within the starch fiber is that it permits a high retention in paper and paper-like webs of synthetic fibers (such as rayon, acrylic, polyester, nylon or polypropylene). Most of these fibers carry very low surface charge and therefore their retention in commonly used latex binder systems, which rely upon precipitation and fiber deposition techniques, are poor. Such poor retention can result in low binder efficiency and problems with foam, sticking and accumulation of polymer in the system. The resin encapsulating starch fiber insures efficient retention and provides the desired end sheet properties.

An additional feature of the present invention is that the starch fibers may also be employed in the production of dry laid nonwovens of synthetic fibers. In such applications, a web is produced using air as the medium for depositing the fibers on a moving wire. Since the synthetic fibers are not hydrated, bonding is inhibited and relatively weak and soft structures are produced. Thus, in order to provide integrity to the web, it is necessary to spray a binder on its surface. In accordance with the present invention, it is possible to blend dry starch fibers with the synthetic fibers. Such a method would be particularly advantageous in the area of dis-

posable nonwovens wherein the biodegradable properties of the starch fiber would be superior to those obtained with the presently employed synthetic fiber binders. As binders those fibers particularly high in amylopectin content are preferred. It is to be noted that the starch fiber may be retained in the final non-woven web or removed therefrom if desired. If the starch fiber is to be removed, as for example, from a ceramic web, exposure to ashing conditions sufficient to burn off the starch fibers provides a suitable means for removal thereof.

The starch fibers, filled or unfilled, may be successfully used alone in the formation of an all-starch paper product or may be utilized in conjunction with all types of cellulosic or non-cellulosic fibers. The hardwood or softwood cellulosic fibers which may be used include bleached and unbleached sulfate (kraft), bleached and unbleached sulfite, bleached and unbleached soda, neutral sulfite, semi-chemical groundwood, chemi-groundwood and any combination of these fibers. These designations refer to wood pulp fibers which have been prepared by means of a variety of processes which are conventionally used in the pulp and paper industry. In addition, synthetic cellulosic fibers of the viscose rayon or regenerated cellulose type can be used, as well as recycled waste papers from various sources. Similarly, ceramic fibers, glass, asbestos or other inorganic fibrous materials may be employed in conjunction with the starch fibers of the invention.

Due to the water-insensitive nature of the starch fibers employed herein, the fibers disperse readily to form stable dispersions which may be used in ordinary papermaking operations without adding surfactants. This permits the use of the fibers in paper making operations and machinery without modification of the usual processing conditions. Thus, fibers may be added to the beater or a blending chest into the head box onto the screen of a Fourdrinier machine and from there the sheet may be carried to the wet press through drier rolls, calenders, and wound up as a sheet without modifying substantially the normal operating characteristics of the machines as used for making cellulose paper. It will be appreciated that in the case of paper made entirely from starch fibers, it may be desirable to place the web between nylon mesh screens or to blot the web drier than is common in conventional operations in order to prevent sticking of the fibers in the drier.

Furthermore, the papermaking operations may be integrated with the starch fiber production operation by employing the slurry containing the fibers as they are precipitated. It is also possible to form shaped articles directly from thick fiber slurries by slush-molding in patterns or molds.

It will be obvious to those skilled in the art that the specific starch employed and the amount of starch fiber used will vary according to the desired quality paper. Thus, we have found that the choice of the proper type of starch makes it possible to achieve selected sheet properties previously achieved only by hydrating and fibrillating wood pulp to various degrees of freeness. Specifically, it has been necessary to lightly refine pulp (650 ml. CSF) in unbleached kraft linerboard applications to insure rapid water removal rates while maintaining high processing speeds. The degree of refining is controlled also by the internal bond strength of the product being produced. The introduction of starch fiber enables rapid water removal and maintenance of production speed but still insures the development of internal bond strength. Glassine papers are frequently

processed from pulp that has been refined extensively (less than 50 ml. CSF). We have now found that glassine type papers can be produced by reducing the cellulose refining in half by adding as little as 15% starch fiber. Alternatively, for papers which require even lower opacity and porosity, it will be preferable to use starch fibers in larger quantities, i.e. about 50% or more.

The starch fiber containing papers of the present invention may be manufactured together with any commonly employed internal additives such as sizes, wet and dry strength additives, etc. or may be surface treated by coating, spraying or saturating as is conventional in the trade.

The starch fiber-containing paper of the present invention can be repulped and recycled. The ability of the starch fiber itself to retain its fiber integrity during a repulping process is influenced by the starch fiber type (higher amylose starches repulp more readily) and the repulping conditions to which it is subjected. Generally, the lower the usage of basic chemicals and elevated temperatures during the repulping operation, the more favorable the recycling of the starch fiber.

The following examples will serve to more fully explain the various aspects and embodiments of the present invention. In the examples, all parts are by weight unless otherwise indicated.

EXAMPLE 1

A slurry was prepared by mixing a naturally occurring unmodified starch composed of 70% amylose and 30% amylopectin in water at a level of 5%, by weight, solid starch and then adding with agitation, a 25% solids solution of sodium hydroxide sufficient to provide a level of 40% caustic on the starch on a dry basis. This mixture was agitated until a dispersion of the starch granules was obtained.

The resultant dispersion was introduced at a pressure of 703 gms/sq. cm. into an agitated coagulation bath consisting of 28% solids ammonium sulfate through a spinnerette containing 100 apertures, each of which had a diameter of 70.2 microns, at an angle of 90° to the moving salt solution. The resultant fibers were collected on a wire mesh screen, washed free of salt and recollected. The fibers possessed an average diameter of 65 microns, an average length of approximately 4 mm., and a final solids content of 23.5%, by weight.

A series of handsheets were prepared on a Noble and Wood sheet mold, from varying levels of bleached softwood pulp (BSWK) in combination with the above prepared fibers. The sheets were dried on the Noble and Wood dryer at a drum temperature of 121° C. and then allowed to condition for a period of 24 hours under constant 22° C. temperature and 55% relative humidity.

Table I summarizes the pertinent sheet making conditions and test data.

TABLE I

Fiber Blend	Basis Weight		Canadian Standard		Shelf-life
	Starch	gms/sq. m.	Freeness (ml) ⁽¹⁾	Porosity ⁽²⁾	Z-directional Strength ⁽³⁾
BSWK	Fiber				
100	0	78.1	544	218	596
90	10	82.6	540	192	630
75	25	80.4	475	74	846
50	50	77.9	367	28	1050+

TABLE I-continued

Fiber Blend		Basis Weight	Canadian	Sheffield	
BSWK	Starch Fiber	gms/sq. m.	Standard Freeness (ml) ⁽¹⁾	Porosity ⁽²⁾	Z-directional Strength ⁽³⁾
25	75	77.1	250	16	1050+

⁽¹⁾Measure of the drainage of water from the pulp through a wire screen. Unbeaten pulps have a high freeness relative to low freeness of well beaten pulps. TAPPI test T227-M-58.

⁽²⁾This test measures the air resistance of paper. Specifically, it measures the volume of air that can be passed through a specific sample area at a given pressure and time. The higher the test value, the more porous the sheet (Used 7.62 cm. I.D. ring; values are unitless).

⁽³⁾The Scott Internal Bond Tester measures the Z-directional strength of paper. This method is designed to determine the average force in joules per square meter required to separate a paper specimen. TAPPI RC-305.

The results shown in the Table indicate that the presence of increasing amounts of this particular starch fiber prepared at a 5% solids dispersion level extends the water holding capabilities of the fiber blend and produces a sheet that is less porous and of higher Z-directional strength than a 100% cellulose sheet.

EXAMPLE 2

Starch fibers were produced using the materials and method employed in Example 1, however, after the final wash, the fibers were dispersed in ethanol solution, collected and allowed to dry. The fibers were then combined with cellulose and handsheets prepared as in Example 1. Tests performed on these handsheets show that the dried fiber provided performance characteristics comparable to those obtained by the moist fibrous products of Example 1.

EXAMPLE 3

Starch fibers were produced using the materials and methods employed in Example 1, however, the starch solids concentration of the starch dispersion was 20% and the final solids level in the fiber was 38%. Handsheets were prepared and tested as in Example 1. The results are shown in Table II.

TABLE II

Fiber Blend		Basis Weight	Canadian	Sheffield	
BSWK	Starch Fiber	gms/sq. m.	Standard Freeness (ml)	Porosity	Z-directional Strength
100	0	86.2	505	158	538

TABLE II-continued

Fiber Blend		Basis Weight	Canadian	Sheffield	
BSWK	Starch Fiber	gms/sq. m.	Standard Freeness (ml)	Porosity	Z-directional Strength
90	10	82.9	545	333	527
75	25	82.9	595	1,215	565
50	50	79.7	676	8,645	647
25	75	79.7	814	50,496	1035+

As illustrated in Table II, the use of starch fibers prepared from a higher solids level dispersion resulted in an increase in the water releasing ability of the furnish (i.e., the freeness), and provided a more porous sheet of greater porosity and Z-directional strength than a 100% cellulose sheet. It is to be noted that this starch level produced freeness and porosity values which distinctly contrast from the values obtained in Example 1 wherein a 5% starch solids level was used to produce fibers. This comparison illustrates the adaptability of the method of the present invention to the production of a variety of properties in the final paper product (e.g., the level of porosity required in a glassine stock versus that required in filter paper). It is also to be noted that in both Example 1 and 3, the strength of the paper was improved by the use of starch fibers.

EXAMPLE 4

Starch fibers were prepared using a 20% solids starch dispersion as in Example 3 except that after washing they were reslurried in ethanol, recovered and dried. Handsheets were prepared and tested and showed that the dried fiber provided performance characteristics comparable to those obtained using the moist fibrous product of Example 3.

EXAMPLE 5

This example illustrates the use of fibers formed from a variety of starch bases in the production of paper according to the present invention.

Starch fibers were prepared and combined with cellulose using the methods described in Example 1. The cellulose portion was beaten to a Canadian Standard Freeness of 645 ml prior to being blended with the starch fiber and the basis weight of the handsheets was maintained at 97.5 gms/sq. m.

TABLE III

Fiber Blend			Tensile ¹	Mullen ²	Z-directional ³	MIT ⁴
BSWK	Starch Fiber	Base	gms/cm ²	gms/cm ²	Strength	Fold
100	0	—	1040.55	4429.40	145	552
90	10	Aminoethylated corn	1462.4	6679.26	903	1,210
70	30	Aminoethylated corn	1476.46	5624.64	1050+	1,280
90	10	Waxy maize	1525.68	6679.26	853	1,670
70	30	Waxy maize	1413.19	5062.17	1050+	1,125
90	10	Unmodified corn	1553.80	5484.02	567	1,340
70	30	Unmodified corn	1293.66	3445.09	1050+	1,245
90	10	Hybrid corn containing 70% amylose	1659.26	5273.10	622	1,420
70	30	Hybrid corn containing 70% amylose	1652.23	4148.17	1050+	1,390
90	10	Amylose	1545.99	5413.71	683	1,433

TABLE III-continued

Fiber Blend		Tensile ¹ gms/cm ²	Mullen ² gms/cm ²	Z-directional ³ Strength	MIT ⁴ Fold
BSWK	Starch Fiber				
70	30 Amylose	1652.23	4780.94	1050+	1,395

¹TAPPI method T404-5s-66 - Determines the tensile breaking strength in pounds per inch (converted to metric units).

²TAPPI method T403-ts-63 - The hydrostatic pressure in pounds per sq. inch (converted) required to rupture the paper when the pressure is applied at a controlled increasing rate through a rubber diaphragm to a circular area 3048 cm. in diameter.

³As defined in Example 1.

⁴TAPPI method T423M-50. The number of folds that the test specimen can endure prior to breaking using a fold tester of the type developed at the Massachusetts Institute of Technology.

As shown in Table III the addition of any of the various starch fibers may be used to improve particular strength properties of the paper when compared with the 100% cellulose fiber sheet.

EXAMPLE 6

This example illustrates two methods for the production of a 100% starch fiber sheet.

Method A. Six grams of unmodified corn starch fibers were slurried in 1 liter of water. The fibers were agitated with a paddle stirrer until a uniform mixture was obtained. A handsheet was formed on the Noble and Wood sheet former that had been fitted with a 100 mesh wire screen. The resultant fibrous web was removed from the screen and blotters and subjected to a series of pressing operations: 3 presses at 7030.8 gms/cm² and 3 presses at 28123.2 gms/cm² with changing of the blotters between pressing operations. The resulting mat solids was 70%. The web was then placed between blotters and dried on the Noble and Wood dryer at 120.1° C. The resultant rigid self-supporting paper-like product had a basis weight of 145 gms/sq.m.

Method B. Starch fibers were processed as described in Method A and the resultant web mat was subjected to a pressing sequence of: 2 presses at 7030.8 gms/cm² and 2 presses at 14061.6 gms/cm² with changing of the blotters between pressing operations such that the resultant wet mat solids was 50%. The web was placed between two nylon wire screens and passed through the Noble and Wood dryer at 120.1° C. The resultant rigid self-supporting paper-like web had a basis weight of 145 gms/sq.m.

EXAMPLE 7

Handsheets were prepared by the method of Example 1 except that commercially unmodified refined glassine stock at two freeness levels was combined with corn starch fibers. The cellulose pulp was obtained from two points in the refinery operation such that one portion had a Schopper Reigler freeness of 350 ml. while the fully refined portion had a 160 ml. freeness. Starch fiber was substituted at the 20% level and all handsheets were prepared at a basis weight of 48.8 gms/m². The sheets were then surface sized on a laboratory size press fitted with rubber rolls using a 1% solids polyvinyl acetate solution (available from Air Products and Chemicals under the tradename Vinol 165) maintained at 60° C. such that a 1% pick-up of polyvinyl acetate

was obtained. The sheets were then conditioned under constant temperature of 20° C. and room humidity 55% for 24 hours prior to being tested for terpentine resistance using TAPPI standard T454-ts-66. The results of the terpentine testing are shown in Table IV.

TABLE IV

Cellulose S.R. Freeness*	Parts	Starch Fiber	Sheet Mold Drain Time	Stock Temp. °C.	Terpentine Test
350 ml	100	—	21.3 secs.	24	855 secs.
350 ml	80	20	19.9 secs.	24	1800+ secs.
160 ml	100	—	62.1 secs.	60	1800+ secs.

*Schopper-Reigler Freeness Tester supplied by Testing Machines, Inc.

The use of starch fiber in combination with partially refined pulp increased the terpentine resistance of that pulp alone and matched the resistance of a fully refined glassine stock. In addition, the refining reduction enabled drain time reductions by a factor of almost 3 fold at significantly lower temperatures. Thus while it is necessary to elevate conventional stock to temperatures of about 60° C. in order to obtain drainage in 62 seconds, drainage in about 20 seconds can be achieved at temperatures of 24° C. with no loss in desirable properties using the method of the present invention. The improved drainage can result in faster machine speeds and efficiency of production while realizing considerable savings in energy due to reduced refining and stock temperatures.

EXAMPLE 8

This example illustrates the improvement in properties obtainable by the incorporation in cellulose pulp of starch fibers containing polymeric microspheres.

Starch fibers were prepared using the method of Example 1 but also incorporating into the starch dispersion, prior to fiber formation, 8.5% microspheres (available from Dow Chemical as XD 6850). The fibers were then incorporated into handsheets in combination with cellulose wood pulp using the method described in Example 1. In all cases, the Canadian Standard Freeness value was 730 ml. for the cellulose component. The results of testing are shown in Table V. As a means of comparison, samples were also prepared in which the microspheres were added directly to the paper pulp as is conventional practice in the industry.

TABLE V

Fiber Blend		% Spheres		Basis Weight gms/sq.m.	Caliper ¹ 1 × 10 ³ cm.	Taber ² Stiff- ness	Z-directional ³ Strength
BSWK	Starch Fiber	Added	In Sheet				
100	0	0	0	97.6	18.79	3.7	111
100	0	0	0	130.1	24.38	6.3	137
100	0	1.8	.86	97.6	24.39	6.6	103
100	0	2.0	1.0	97.6	25.40	7.1	90

TABLE V-continued

Fiber Blend	% Spheres		Basis		Taber ²		Z-directional ³
	Starch Fiber	In Sheet	Weight gms/sq.m.	Caliper ¹ 1 × 10 ³ cm.	Stiffness	Strength	
BSWK							
95	5	.43	.43	97.6	23.11	5.0	168
90	10	.86	.86	97.6	26.16	6.3	206
85	15	1.29	1.29	97.6	28.45	7.5	237

¹Thickness of paper expressed in thousandths of a centimeter²TAPPI Method T451-M-60³As defined in Example 1.

As illustrated in Table V, the introduction of the microspheres by either of the methods substantially improved both the caliper and stiffness of the paper product. In this regard, it was possible by the addition

(2). In all cases the basis weight of the sheet was 97.6 g/sq.m.

The physical and optical properties of the resulting paper sheets are shown in Table VI.

TABLE VI

Conventional Addition			Starch Fiber			Z-directional ⁽³⁾ Strength	
% Cellulose	% Clay	% TiO ₂	% Starch	% Clay	Opacity ⁽¹⁾		Tensile ⁽²⁾
100	0	0	0	0	85.9	991.34	302
87.2	12.8	0	0	0	92.0	625.74	113
75.2	0	0	5.0	19.8	88.9	1371.00	351
68.4	6.8	0	5.0	19.8	90.5	864.79	256
72.1	0	4.5	4.7	18.7	94.1	850.73	233

⁽¹⁾TAPPI method T425-m-60. Expressed in percent and defined as 100 times the ratio of the diffuse reflectance of a specimen backed with a blank of no more than .005 reflectance of the same specimen backed with a white body having an absolute reflectance of 0.89. The higher the value the more opaque the paper.

⁽²⁾Defined in Example 5.

⁽³⁾Defined in Example 1.

of microspheres to achieve the caliper and stiffness of 130 g/sq.m. basis weight at a level of only 97.6 g/sq.m. The weight saving, both in amount of fiber required and in related costs recognized after production of the paper (e.g. mailing), are readily recognizable.

When the other properties obtained from the microsphere containing sheets were compared, it was found that retention of the externally added spheres was approximately 50% of the amount initially added while the retention was approximately 100% for those added in the encapsulated fibers. Moreover, there was a decrease in strength and evidence of non-uniform distribution of the spheres (with a greater concentration on the felt side) in the case of the externally added spheres while these factors were not present in the case of the starch encapsulated spheres. Thus, the increase in caliper and stiffness observed using the conventionally employed external addition of the spheres was obtained only at the expense of decreasing internal bond strength of the paper, while introducing the spheres within the starch fiber insured their retention with the sheet while increasing the internal bond strength in addition to providing the desired stiffness and caliper increases.

EXAMPLE 9

This example illustrates the results obtained using three methods for incorporating clay in paper production.

Handsheets were prepared using methods similar to those described in Example 1. The handsheets were prepared so as to incorporate a number two coating grade clay in the final sheet during the formation process. The incorporation of the clay into the handsheets was accomplished in three different manners: (1) by conventionally slurring the pigment with the pulp fibers, (2) by incorporating starch fibers prepared according to Example 1 but containing 80% clay and 20% starch, and (3) using a combination of methods (1) and

As illustrated in Table VI, incorporating the pigment within the starch fiber enabled higher pigment loadings and strength properties when compared to conventional pigment loading techniques. Thus, when 12.8% clay was added to cellulose pulp using conventional techniques, the tensile and Z-directional strength decreased. In contrast, when 19.8% clay was added in the form of encapsulated starch fibers (a total addition of 24.8%), the tensile and Z-directional strength improved. It is further shown that the reduction in opacity obtained by use of the clay-encapsulated fiber can be compensated for by the external addition of a small amount of clay or of titanium dioxide.

EXAMPLE 10

This example illustrates the superior retention ability of the starch fibers as used in the method of the present invention.

Bleached softwood kraft was beaten to a freeness of 500 ml. Canadian Standard and divided into three portions. To one portion, a No. 2 coating grade clay was added and the resultant blend agitated until the pigment was uniformly distributed throughout the pulp fibers. Another portion was treated in the same manner except that Natron 86 (a trademark of National Starch and Chemical Corporation), a retention aid, was added. To the remaining portion of the pulp, starch fibers containing clay encapsulated therein (50% starch and 50% clay) were added and the fiber blend was agitated until uniform distribution was obtained. Handsheets were prepared by a method similar to Example 1 and the sheets for clay content and percent retention. The results are shown in Table VII.

TABLE VII

Fiber Blend		Clay	Retention Aid	% Clay Retention
BSWK	Starch Fiber (50% Clay)			
90	0	10	0	11
90	0	10	0.02%	35
80	20	0	0	97

As illustrated in Table VII, the retention of clay was highest when the clay was encapsulated in the starch fiber pursuant to the present invention.

EXAMPLE 11

The following example illustrates the use of starch fibers for their binding properties in the production of a multi-ply sheet.

Two-ply handsheets were prepared on a Noble and Wood sheet former from bleached softwood kraft that had been beaten to a 500 ml. Canadian Standard Freeness. To achieve a final basis weight of 146 gms. per square meter, two plies (each approximately 73 gms. per square meter) were prepared and wet pressed together prior to drying on the Noble and Wood drier at 121° C. The control handsheet contained 100% cellulose in both plies, while the test handsheet had 20% of the cellulose in the top ply replaced by starch fiber. The bond between the plies was tested using the Scott Internal Bond tester and the results shown in Table VIII.

TABLE VIII

Fiber Blend	Z-directional Strength ⁽¹⁾
Bottom Ply - Top Ply	
100% Cellulose - 100% cellulose	119.7
100% Cellulose - 80% cellulose and 20% Starch Fiber	197.4

⁽¹⁾Defined in Example 1.

As shown in Table VIII the presence of the starch fiber increased the bond strength between the plies of the final sheets.

EXAMPLE 12

This example shows the production of paper containing a variety of additives incorporated by the addition of starch fibers containing the encapsulated additives.

In a manner similar to that described in Example 8, additives were encapsulated within the starch fibers and used to form handsheets having a given percentage of the starch fibers as indicated in Table IX.

TABLE IX

Additive	% Additive in Starch Fiber	% Addition of Starch Fibers in Pulp
TiO ₂	25	20
CaCO ₃	25	20
Al powder	25	20
Carbon black	25	20
Fibran 68	5	10
(A trademark for a sizing agent available from National Starch and Chemical Corporation)		
Pexol 200	5	10
(A trademark for a sizing agent available from Hercules Powder Co.)		
A 1:1 blend of antimony trioxide and vinyl chloride homopolymer (fire retardant)	50	50
Tris-dichloro-propyl phosphate	57	40

TABLE IX-continued

Additive	% Additive in Starch Fiber	% Addition of Starch Fibers in Pulp
(fire retardant)		

In all cases, the additives were retained at a high level in the final paper product and imparted their characteristic property thereto.

EXAMPLE 13

This example illustrates the use of the starch fibers as a means to incorporate latex binders in a nonwoven web of synthetic fibers.

A dispersion of rayon fibers (0.635 cm, 1.5 denier) and polyester fibers (0.635 cm, 1.5 denier) were prepared at 0.1% solids in separate containers.

A 100% starch fiber product as well as a starch fiber that contained 20% on a weight basis of encapsulated latex, vinyl acetate/butyl acrylate copolymer, were added as binders in amounts such that the final fiber blend would contain 25% of the starch fiber products. Handsheets were prepared on a Noble and Wood sheet former at a basis weight of 65 gms. per square meter using methods similar to those described in Example 1. The webs were tested to determine tensile strength improvement and the results summarized in Table X.

TABLE X

Starch Fiber Description	Binder Level	Synthetic Fiber	Tensile ⁽¹⁾ (gms/cm ²)
None (control)	—	Rayon	*
None (control)	—	Polyester	*
100% Starch	25%	Rayon	710.11
100% Starch	25%	Polyester	217.95
80% Starch - 20% latex	25%	Rayon	984.31
80% Starch - 20% latex	25%	Polyester	135.69

*Sheet did not possess sufficient integrity to measure tensile

⁽¹⁾Defined in Example 5.

As shown in Table X, webs prepared using both the starch fibers and the starch-latex fibers as binders possessed superior tensile strength. In contrast, control webs prepared from 100% synthetic fiber did not possess sufficient integrity to even be handled for testing. It is noted that the particular latex employed increased the tensile strength of the rayon web while decreasing the strength of the polyester web compared to the 100% starch fiber. This illustrates the necessity of choosing the proper latex for the synthetic fiber being treated.

EXAMPLE 14

This example illustrates the use of starch fibers as binders with ceramic fibers. The example also shows that the starch fiber binders may be removed after formation of the web resulting in the production of a 100% ceramic fiber sheet.

A 3% solids ceramic fiber slurry was prepared in a Waring Blender and agitated for 1 minute after 0.2% NaOH (dry basis based on the weight of the fiber) was added to serve as a dispersing agent. The fiber mix was then transferred to a container that was equipped with a paddle stirrer and a pre-determined amount of starch fiber added from a 1% solids mix. After mixing the blend for a period of 5 minutes, handsheets were prepared at 407 gms/square meter basis weight, on the Noble and Wood sheet former. As a control, a ceramic sheet was made without the addition of any starch fi-

bers. All sheets were subjected to strength tests with the results shown in Table XI.

TABLE XI

Starch Fiber	Basis Weight, gms/sq. meter	Tensile ⁽¹⁾ gms/cm ²
0	407.5	—
5%	407.5	3.52
10%	407.5	20.39

*Sheet did not possess sufficient integrity to measure tensile
(¹) Defined in Example 5.

The sheets containing the starch fibers were then placed in a kiln maintained at a temperature sufficient to ash the starch fibers and fuse the ceramic fibers. A well bonded ceramic web was thereby produced.

EXAMPLE 15

Two ply handsheets containing 10% TiO₂ on the final sheet weight of approximately 145 gms/sq.m. were prepared. In the control handsheets, TiO₂ was added in the conventional manner by dispersing the pigment with those unbleached kraft fibers which comprised the top liner. In the remaining handsheets, 20% TiO₂ encapsulated starch fiber on a weight basis was added in sufficient quantity to the top liner to provide 10% TiO₂ on the final sheet weight.

The final sheet was constructed from two plies, each prepared separately on the Noble and Wood sheet mold at approximately 72.5 gms/sq.m., removed from the wire and pressed together in the wet mat state at 14061.6 gms/cm². The sheets were then dried on the Noble and Wood drier at 121° C. Brightness readings were taken on the top liner side in accordance with TAPPI standard R452-M-58 with the results indicated in Table XII.

TABLE XII

Sample Sheet	Top Liner Brightness
Control	26.2
Starch Fiber	30.1

The results shown in Table XII indicate that the handsheets prepared using the TiO₂ encapsulated starch fibers had superior properties to those prepared using conventional methods.

The preferred embodiments of the present invention having been described above, various modifications and improvements thereon will now become readily apparent to those skilled in the art. Accordingly, the spirit and scope of the present invention is to be limited not by the foregoing disclosure, but only by the appended claims.

We claim:

1. In a process for manufacturing paper and paperboard comprising the steps of introducing an aqueous slurry of a fibrous pulp material onto a screen in such a manner that the water is removed thereby forming a sheet of consolidated fibers which, upon pressing and drying, yields the final paper product, the improvement comprising the step of replacing from 1 to 100% by weight of said pulp material with water-insensitive starch fibers of 10 to 500 microns in diameter, said fibers being produced by extruding a thread-like stream of a colloidal dispersion containing starch at 5-40% by weight solids, wherein said starch is present in an amount more than 50% by weight of the fiber forming ingredient, into a moving coagulating bath comprising an aqueous solution of a coagulating salt selected from

the group consisting of ammonium sulfate, ammonium sulfamate, mono-basic ammonium phosphate, di-basic ammonium phosphate and mixtures thereof, the solution containing the coagulating salt in an amount at least sufficient to coagulate the starch, said starch fibers further characterized in retaining fiber integrity when dispersed in an aqueous medium.

2. The process of claim 1 wherein the starch fibers are prepared from corn starch or waxy maize starch.

3. The process of claim 1 wherein the starch fibers are prepared from high amylose starch.

4. The process of claim 1 wherein the starch fibers are prepared from cationically derivatized starches.

5. The process of claim 1 wherein the starch fibers are prepared from ether or ester derivatives of starch.

6. The process of claim 1 wherein the colloidal starch dispersion additionally includes clay or pigment replacing said starch in an amount up to 80% by weight.

7. The process of claim 1 wherein the colloidal starch dispersion additionally includes a water-insoluble additive selected from the group consisting of microspheres, metallic powders, latices, oils and plasticizers replacing said starch in an amount less than 50% by weight.

8. The process of claim 1 wherein the colloidal starch dispersion additionally includes a dispersed hydrocolloid replacing said starch in an amount less than 50% by weight.

9. The process of claim 1 wherein the starch fibers have a length of 0.1 to 3.0 mm.

10. The process of claim 1 wherein the remaining fibrous pulp material is substantially in the form of wood cellulose.

11. The process of claim 1 wherein the remaining fibrous pulp material is substantially in the form of fibers selected from the group consisting of polyester fibers, rayon fibers, ceramic fibers, glass fibers and asbestos fibers.

12. The process of claim 1 wherein 1-50% by weight of the fibrous pulp is replaced by water-insensitive starch fibers.

13. The process of claim 12 wherein at least a portion of said unreplaced fibrous pulp has been refined to a Schopper Reigler freeness of between about 350 ml. to 160 ml., and said final paper product having glassine greaseproof properties.

14. The paper or paperboard composition produced by the process of claim 1.

15. The paper and paperboard compositions of claim 14 wherein at least one water-insoluble additive is encapsulated within the starch fiber.

16. The paper of claim 14 wherein 1-50% by weight of the papermaking cellulose pulp fibers is replaced by water-insensitive starch fibers.

17. The paper of claim 14 wherein 1-50% by weight of the papermaking cellulose pulp fibers is replaced by water-insensitive starch fibers and at least a portion of said unreplaced papermaking cellulose pulp fibers has been refined to a Schopper Reigler freeness of between about 350 ml. to 160 ml.

18. A process for incorporating water-insoluble additives within an aqueous papermaking slurry of a conventional papermaking system comprising the steps of thoroughly dispersing at least one water-insoluble additive in a colloidal dispersion containing starch at 5-40% by weight solids, wherein said starch is present in an amount more than 50% by weight of the fiber forming ingredient, and precipitating said dispersion by extruding a thread-like stream of the dispersion into a moving

coagulating bath comprising an aqueous solution of a coagulating salt selected from the group consisting of ammonium sulfate, ammonium sulfamate, mono-basic ammonium phosphate, dibasic ammonium phosphate and mixtures thereof, the solution containing the coagulating salt in an amount at least sufficient to coagulate the starch so as to form water-insensitive starch fibers

encapsulating said additive; and subsequently using the resulting starch fibers as a component in a papermaking pulp system, said starch fibers further characterized in retaining fiber integrity when dispersed in an aqueous medium.

* * * * *

10

15

20

25

30

35

40

45

50

55

60

65